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PHYSICAL REVIEW

NEW PRECISION IN COSMIC RAY MEASUREMENTS; YIELDING EXTENSION OF SPECTRUM AND INDICATIONS OF BANDS

By R. A. Millikan and G. H. Cameron

Abstract

Method of measurement of capacities of the order of one cm.—A method is described which leads to greatly increased precision in the measurement of capacities of the order of one electrostatic unit.

More penetrating cosmic rays than we have previously found are indicated by a new absorption curve obtained in Gem Lake (9080 ft.) and Lake Arrowhead (5125 ft.) with much greater precision than hitherto possible.

Cosmic-ray spectrum.—The new curve affords definite evidence for the existence of bands in the spectrum of cosmic rays. The measurements indicate that the cosmic rays consist chiefly of two bands about three octaves apart of mean absorption coefficients 0.35 and 0.04 to 0.05 per meter of water.

The total energy of cosmic rays at the top of the atmosphere is found to be very nearly one-tenth that due to starlight and heat as computed from Seares' data.

I. Introductory

UNTIL about a year ago we had been so occupied with the exploratory phase of the cosmic-ray work, that is, with testing on a given instrument for variations with altitude, with direction, with geographical position, with penetration through absorbing materials, etc., that we had had little time to devote to improving the precision of measurement, and our own former electroscope readings have not yet shown a consistency and a duplicability which was as good as we thought obtainable. Also with two different electroscopes which we have designated as No. 1 and No. 3, we have obtained under the same conditions 1.4 and 1.6 ions per cc per sec. respectively, as the value of the sea-level ionization due to the cosmic rays. Such differences, whatever their cause, are tolerable only in the initial phases of work on any given physical quantity.

Further, when the findings of different observers on any cosmic-ray constants are compared the differences are more striking than the agreements. At high altitudes Millikan and Bowen got a total discharge of an electroscope about one-fourth that computed from the curves of Kolhörster and of Hess; on Pike's Peak we find from our curves 5.2 ions per cc per sec. per atmosphere due to cosmic rays, while Swann publishes 0.75 ions per cc per sec. per

atmosphere in the same spot; at sea-level Kolhörster and most observers following him still take 2 ions per cc per sec. as the cosmic-ray ionization in the atmosphere, while we publish the value 1.4. Such differences are quite like those found, for example, in the early determinations of e/m which showed fluctations of 100%, but they cannot long be permitted.

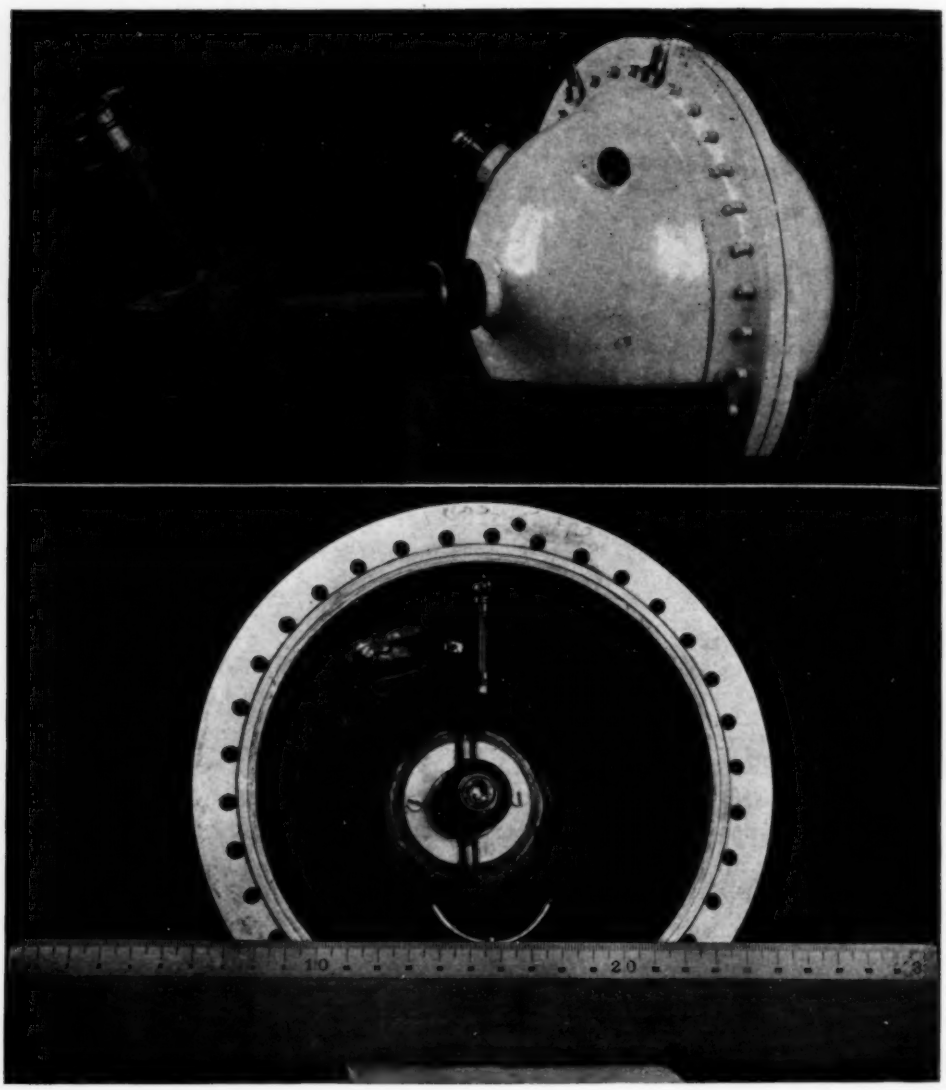

Fig. 1. Photographs of electroscope.

Upon our return from Bolivia in September, 1926, we at once set at work to endeavor to improve our instrumental technique with a view to initiating in our own work at least a period of something like precision measurements on cosmic-ray effects.

II. Precision in Cosmic-Ray Electroscopes

The uncertainties in our own preceding absolute determination of cosmic-ray ionization have been due (1) to lack of precision in the measurement of capacities of the order of one electrostatic unit, (2) to lack of electroscope sensibility and (3) to irregularities due to difficulties in eliminating "soaking-in" effects.

In the new electroscopes, designed primarily for under-water work at depths of many meters, we have used the spherical form as shown in Fig. 1. The volume is about one and a half liters, accurately 1.58 l; the wall-material is steel of thickness 0.6 mm. The heavy flanges, 7mm thick, on each hemisphere are bolted together by 34 bolts with the aid of which a tongue 2 mm high, 3 mm wide, and running entirely around the face of one flange is squeezed into a groove in the face of the other flange. At the bottom of this groove is a rubber washer. This renders the sphere completely air-tight, so that the pressure within it may be pumped up to many atmospheres, thus increasing largely the sensibility. The fibers are of quartz, platinized by cathode sputtering. They are attached as in our preceding electroscopes, save that the upper quartz supporting rod is quite small (2.1 cm long, 2 mm diam.) so as to reduce "soaking-in" effects. The charging is done by a little electromagnetic plunger operated by a battery current entering the coil through the two electrodes just visible inside the opening seen in the face of the sphere in Fig. 1. The device is sketched in Fig. 2.

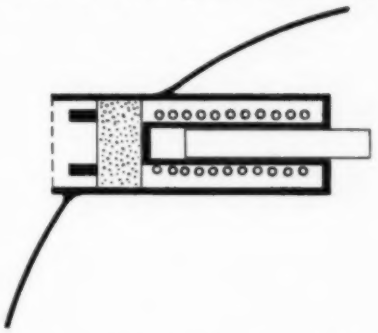

Fig. 2. Device for charging the electroscope.

The most important element in the design is found in the simple method used for measuring the capacity of the electroscope, a method capable of determining a capacity of the order of one electrostatic unit with an accuracy of about one part in a thousand. It is easily intelligible from Fig. 3. After the fibers have been mounted in the face of the hemisphere that carries their supports, there is screwed on in place of the other permanent hemisphere a third, dummy hemisphere just like the permanent one, save that it carries the cylindrical projection shown in cross-section in Fig. 3.

With this dummy hemisphere the steps in the process of finding the capacity of the fibers are then as follows: Two thin and perfectly straight steel wires are taken 1.06 mm in diameter, but one exactly 6 cm longer than the other. Each of these is ground slightly conical at one end and that end can be tightly pressed into a little conical hole in the minute brass piece to which the fibers are attached at the top, thus adding to the capacity of the fibers alone the capacity of this wire (or "cylindrical condenser") in one or the other of the positions shown in Fig. 3. After the careful centering of the wire, both cylindrical condensers may be closed by an accurately fitted cap of an

inner diameter precisely the same as that of the cylinders. A constant source of gamma rays is placed a couple of meters away and, when neither of the wires is in place, the time t_1 of discharge through, say, twenty scale divisions is noted. The short steel wire is then inserted and centered as shown in the right-hand diagram of Fig. 3, the cap put on, and the time t_2 of discharge

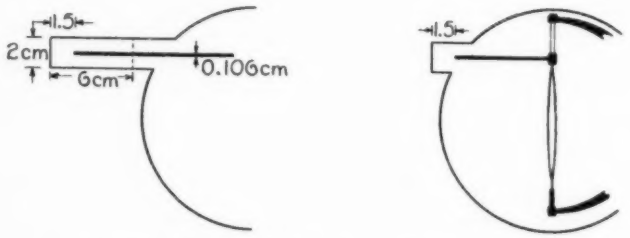

Fig. 3. To illustrate method of measuring capacities.

through the same range is again taken. Then the long steel wire and the long cylinder each having 6 cm of additional length, replace the shorter ones. After the centering of the wire, the cap of the long cylinder is put on, thus assuring that the "end effect" is precisely the same with the long wire and cylinder as with the short ones. Then the time t_3 of discharge through the same twenty divisions is again taken. The capacity x of the fibers alone is then easily seen to be given by

$$x = ct_1/(t_3 - t_2)$$

in which c, the capacity of the added 6 cm of cylindrical condenser is given by

$$c = \frac{1}{2}\frac{l}{\log_e(a/b)} = \frac{1}{2}\frac{6}{\log_e(2/0.106)} = 1.019 \text{ e.s.u.}$$

It is obvious not only that this method eliminates completely the end effect, but that, if dimensions are so chosen that t_1 is about equal to $(t_3 - t_2)$ the accuracy may be made very high. The volume of air in the added cylindrical condenser has been neglected in the foregoing analysis since it is small, but it can of course be easily taken into account if desired, the time t_3 being multiplied by the ratio of the volume without the long cylinder to the volume with it, for the sake of reducing all three t's to conditions of equal volumes.

III. New Depth-Ionization Curve

With the foregoing electroscope pumped up to a pressure of about 8 atmospheres and therefore having a sensibility, for these very hard rays, about eight times as great as we had used in preceding under-water work, the depth-ionization curve shown in Fig. 4 was plotted from readings taken in Arrowhead Lake (140 ft. deep) and in Gem Lake (225 ft. deep) and tabulated in Table I.

Although the elevations of Arrowhead and Gem Lakes are 5,100 ft. and 9,080 ft., respectively, and the latter 250 miles north of the former, as in the case of all our former under-water work, when the rates of discharge are

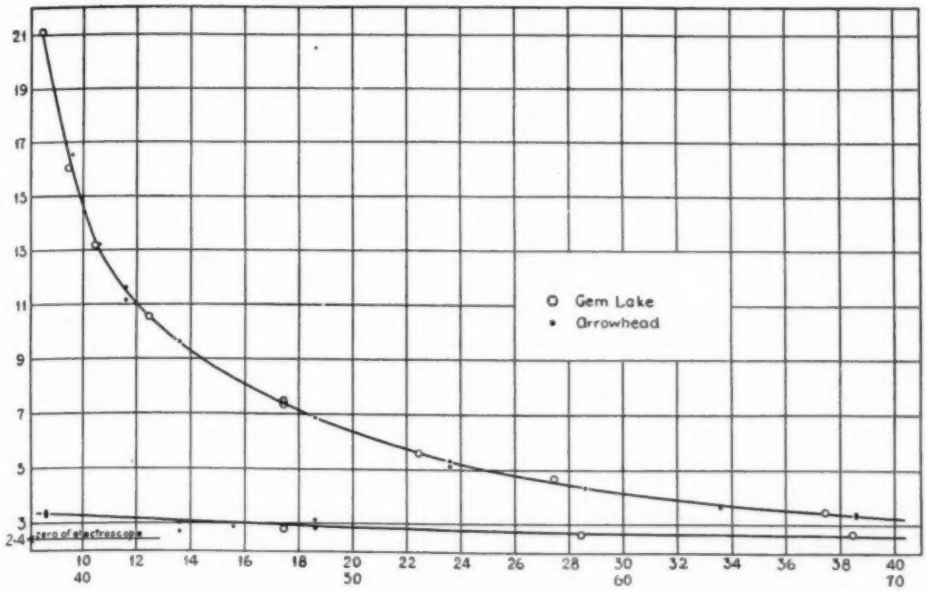

Fig. 4. Depth-ionization curve. Ordinates: Cosmic-ray ionization in ions per cc per second. Abscissas: Depth beneath top of atmosphere in equivalent meters of water. Lower curve: Continuation of upper between 40 and 70 meters.

plotted against depth in equivalent meters of water beneath the top surface of the atmosphere, *the readings all fall upon a smooth ionization-depth curve* (see Fig. 4). Also in spite of the fact that the reading at any particular depth

TABLE I. *Ionization in ions per cc per sec. at various depths below surface of the atmosphere. Readings taken in Arrowhead and Gem Lakes.*

Depth below surface of atmosphere	Arrowhead	Gem	Depth below surface of atmosphere	Arrowhead	Gem
8.45		21.1	27.45		4.68
9.45		16.07	28.6	4.37	
9.6	16.52		33.6	3.63	
10.45		13.19	37.45		3.47
10.6	13.22		38.6	3.36, 3.38, 3.38	
11.6	11.17, 11.65		43.6	2.68, 2.98	
12.45		10.56	45.6	2.87	
13.6	9.64		47.45		2.79
17.45		7.35, 7.48	48.6	2.83, 3.12	
22.45		5.59	57.45		2.62
23.6	5.33, 5.14		67.45		2.63

is now about eight times greater than in our preceding work (since for these very hard rays ionization is at least roughly proportional to pressure) yet the readings are now seen to show much less spread in ions per cc per sec.

than heretofore, so that the new curve shows that the precision has been multiplied fully tenfold, probably more. Not a single reading was discarded during the taking of this particular series of thirty readings. It will be seen that there are but two points in the thirty that now depart from the curves by as much as four-tenths of an ion, while all save three or four are closer than one-tenth of an ion. The resolving power of this curve is therefore very much greater (say tenfold) than that of any we have heretofore published, and we can now draw more definite conclusions about the spectral distribution of cosmic rays than have heretofore been possible.

IV. Spectral Distribution of Cosmic Rays

The first point to be noted about the present curve is that it goes quite definitely down to a depth of at least 58 meters (190 ft.) before the readings cease to decrease measurably with further immersion. There is, indeed, one erratic reading at 43.6 m but there are eight other consistent ones between 38 m and 48 m, so that the position of the curve in this region is fixed with certainty, while the two consistent readings between 58 m and 68 m show that the curve is measurably decreasing down to at least 58 m. *This means at once that our increased sensibility has brought to light very much harder rays than we had observed before when the readings failed to decrease measurably below 25 m.* How much harder may be determined as follows:

The curve is now sufficiently certain so that it is possible with the aid of the Gold table[1] to analyze it meter by meter. This table gives the value of I/I_0 in which I is the observed ionization at depth h below the top of the atmosphere and I_0 the value at the top, for each value of μh. Inserting two values of h (depth beneath top of atmosphere) a meter apart and the observed

Table II. *Portion of the Gold table used in this work.*

μh	I/I_0	μh	I/I_0	μh	I/I_0
0.01	0.94967	0.45	0.35623	1.5	0.07310
0.02	0.91311	0.50	0.32665	1.6	0.06380
0.03	0.88168	0.55	0.30010	1.7	0.05578
0.04	0.85354	0.60	0.27618	1.8	0.04882
0.05	0.82784	0.65	0.25456	1.9	0.04279
0.06	0.80404	0.70	0.23495	2.0	0.03754
0.07	0.78184	0.75	0.21711	2.2	0.02898
0.08	0.76096	0.80	0.20085	2.4	0.02246
0.09	0.74125	0.85	0.18599	2.5	0.01982
0.10	0.72255	0.90	0.17241	2.6	0.01746
0.15	0.64104	0.95	0.15994	2.8	0.01360
0.20	0.57420	1.0	0.14850	3.0	0.01064
0.25	0.51773	1.1	0.12828	3.5	0.00580
0.30	0.46912	1.2	0.11110	4.0	0.00320
0.35	0.42671	1.3	0.09644	4.5	0.00179
0.40	0.38937	1.4	0.08389	5.0	0.00099
				6.0	0.00032

values of I_1 and I_2 we obtain at once the corresponding μ. For convenience we reproduce in Table II the part of the Gold table which we use in this

[1] Gold, Proc. Roy. Soc. **A82**, 43 (1909).

work, (i.e., for $n = 2^1$). Table III gives the series of values of μ thus obtained for successive values of h from 9.5 m down to 60 m, the lower steps, however, being 5 m or 10 m apart instead of 1 or 2.

TABLE III. *Absorption coefficients at various depths, in meters of water, below top of atmosphere.*

Depth in meters of water beneath top of atmosphere	Absorption coefficient μ	Depth in meters of water beneath top of atmosphere	Absorption coefficient μ
8.45– 9.5	0.22	15–20	0.065
9.5 –10.5	0.20	20–30	0.057
10.5 –11.5	0.11	30–40	0.05
11.5 –12.5	0.09	40–50	
12.5 –15	0.07	50–60	

Before attempting to interpret this table it is important to recall that both at Muir Lake (11,800 ft) and at Lake Miguilla (15,000 ft) we obtained the value[2] $\mu = 0.25$ and also that it was necessary, in order to fit Millikan and Bowen's sounding-balloon measurements,[3] which reached more than nine-tenths of the way to the top of the atmosphere, to assume that up to that height the mean absorption coefficient remained about 0.25, in other words that the cosmic rays consisted of a band of frequencies an octave or more wide which, however, did not extend in appreciable intensity into the region between that for which $\mu = 0.25$ and that of gamma rays.

The present measurements enable us to make still further inferences about the character of this band. The fact that an absorption coefficient of between 0.2 and 0.3 appears to hold from the top of the atmosphere down to a depth of 10.5 m and that in going down 1 meter more the mean μ drops suddenly to 0.11, while in going but 3 meters more it drops to 0.07, obviously means that the cosmic rays are not at all continuously distributed between $\mu = 0.2$ and $\mu = 0.07$. Indeed we find that between 30 m and 60 m one single coefficient viz. $\mu = 0.05$ will reproduce our curve within the limits of observational error, so that at the lower end the cosmic rays are more or less monochromatic. *The sudden change in μ at a depth of about 11 m means that at that point a band of long wave-length, or of relatively large absorption coefficient, is dropping out and one of much shorter wave-length is left to cause the bulk of the ionization.* The suddenness of this change is very illuminating. In the preceding paper we showed that if we assumed a mean absorption coefficient 0.25 to be valid from about 9 m up to the top of the atmosphere we accounted perfectly not only for our own data but also for the Millikan-Bowen results at very high altitudes. In precisely the same way we can calculate these ionizations using now as a starting point the intensity observed at 9 m in this new set of observations. If we now subtract from this curve the theoretical values for $\mu = 0.05$, having the intensity necessary to fit the lower end of the curve (from 30 m down), the differences in the range 9 m to 2 m are fitted to a very rough first approximation by $\mu = 0.35$. But the sum of the

[2] Millikan and Cameron, Phys. Rev. **31**, 163 (1928).
[3] Millikan and Bowen, Phys. Rev. **27**, 353 (1926).

two curves for $\mu = 0.05$ and $\mu = 0.35$ rises above the observed curve in the range between 9 m and 15 m. In other words, this combination of $\mu = 0.05$ and $\mu = 0.35$, while fitting the observed curve well at the lower end (30 m to 60 m) and roughly at the upper end, does not yield so sharp a change of μ in the neighborhood of 10.5 m as is shown in Table I, and yet this is the region in which our observational data are especially reliable. The foregoing sudden change, then, combined with the approximate fitting of the two ends by $\mu = 0.05$ and $\mu = 0.05 + \mu = 0.35$, respectively, requires that the cosmic rays consist chiefly of two bands of wave-lengths even farther apart than correspond to $\mu = 0.05$ and $\mu = 0.35$. No single coefficient much lower than $\mu = 0.05$ will, however, fit the lower part of the curve. We are forced, then, to build up this part of the curve out of components whose joint effect is about that of $\mu = 0.05$, but which contain at least one strong radiation of smaller value of μ than 0.05, for this will tend to sharpen up the "knee" at $h = 10.5$. The net result of this method of inspection and trial is that if we divide the radiation reaching 30 m depth so that two-thirds of it corresponds to $\mu = 0.04$ and one-third to $\mu = 0.08$ we find that we can again fit the lower part of the curve (20 m to 60 m) perfectly. For depths less than 20 m the sum of these two ionization curves is of course much less than the observed ionization. But if we now give the residual ionization at 9 m to $\mu = 0.35$ and from this starting point complete this curve and then add the three curves, we can build up the observed curve everywhere to within about the limits of its experimental uncertainty. Table IV shows how perfectly this particular distribution of frequencies and intensities fits the observed readings. It will be seen that it is only from 9 m up to 2 m that the "sum" departs appreciably from the figures in the last column, and this is the region in which we have no observational data except the reading obtained by Millikan and Bowen in their highest balloon flight which reached an altitude corresponding to about 1 m and had a mean height of about 2 m. If this reading were 30% too high because of (a) observational uncertainty (it might reach nearly this value), or (b) radioactive deposit on the electroscope walls, or (c) soft radiations reaching down a meter or so from the top of the atmosphere, there would be no discrepancies at all between the last two columns. In other words, the departures are not now serious, and they are in the right direction, for while the balloon data may be too high they can hardly be too low.

There is obviously no altogether unique solution to such a curve as that shown in Fig. 4. On the other hand, *every solution must have the approximate characteristics here given*. The sharp "knee" and the characteristics of the curves at the two ends cannot be obtained save by two frequency bands which have their main strength at about $\mu = 0.04$ to 0.05 and $\mu = 0.30$ to 0.40. This conclusion is of course of much importance for the determination of the character of the nuclear changes which give rise to the cosmic rays. It needs checking by new determinations of the ionization-depth curve—determinations which we hope soon to carry out with electroscopes of still greater sensibility—but *the present measurements at least furnish indications that the cosmic rays consist chiefly of three bands for which the mean absorp-*

TABLE IV. *Comparison of the experimental curve with a theoretical curve compounded of three wave-lengths.*

Depth (meters of water)	$\mu=0.04$	0.08	0.35	Theoretical Curve (Sum)	Experimental Curve
70	0.15	0.02		0.17	0.16
60	0.24	0.03		0.27	0.24
50	0.40	0.09		0.49	0.44
40	0.69	0.23		0.92	0.85
30	1.20	0.60		1.80	1.79
20	2.16	1.70	0.10	3.96	3.95
15	2.98	2.96	0.37	6.31	6.24
12	3.64	4.21	1.21	9.06	8.60
10	4.20	5.35	2.65	12.20	12.20
9	4.52	6.07	4.20	14.79	16.05
7	5.27	7.86	9.64	22.77	30.7
5	6.19	10.4	23.9	40.5	61.0
3	7.49	14.1	63.3	84.9	127.5
2	8.21	16.7	107.3	132.2	192.0

tion coefficients are approximately 0.35, 0.08 and 0.04. Computing as we have heretofore done by the Compton formula our shortest wave-length is now 0.00008A, and the equivalent generating potential approximately 150,000,000 volts.

V. COMPARISON OF THE TOTAL ENERGY IN COSMIC RAYS AND IN STARLIGHT

The absolute value of the cosmic-ray ionization at sea-level (10.33 m) inside the present electroscope can be read off with great precision from the foregoing curve. It will be seen to be 11.25 ions per cc per sec. To reduce this to atmospheric pressure we shall provisionally divide through by the pressure, namely 8. This gives 1.4 ions, the value previously found with the use of two other electroscopes. This procedure involves a small error since we have obtained evidence that even for these very hard rays there is not strict proportionality between pressure and ionization. We shall make a later report upon the amount of this uncertainty as experimentally determined. But for the present purpose we shall make no significant error if we take 1.4 as the sea-level ionization at atmospheric pressure, and with this as a starting point compute with the aid of the absorption coefficients given in Table III the ionization as far as this curve goes, namely up to 9.5 m. From there up we have already found by observations up to 15,000 feet in Bolivia that the apparent absorption coefficient does not rise above 0.25, a value which also fits the Millikan and Bowen sounding balloon data up to practically the top of the atmosphere. The ionization at all heights in the atmosphere above 8.5 m can then be obtained with the aid of Table II and $\mu=0.25$, the values thus found being practically identical with those given in a preceding paper.[2] By then plotting the successive values of these ionizations against depth in equivalent meters of water beneath the surface from 0 to ∞, it is easy to make a graphical integration and determine the total ionization due to cosmic rays in a column of water of 1 sq. cm area, and extending from the top of the atmosphere down to say 50 m or 60 m, where the ionization has practically ceased. For such an integration it is important to remember that the number of ions per cc of water at sea-level is 1.4×850, the last factor being

the ratio of the densities of water and air. This factor must of course be inserted at all depths to obtain the total number of ions per sq. cm column. The result is 12,850,000 ions.

Taking the average ionizing potential of the external shell of electrons in nitrogen as 15 volts (if K electrons are ejected K radiation is produced which spends itself in ionizing the outer shell) we find that the average energy required to produce an ion is $(15/300)\times 4.774\times 10^{-10}=2.4\times 10^{-11}$ergs. The total energy content, then, of the cosmic rays coming into the earth per sq. cm is $12.8\times 10^{6}\times 2.4\times 10^{-11}=3.07\times 10^{-4}$ergs.

To compare this with the heat and light coming into the earth from the stars we have the solar constant at the top of the atmosphere $=1.94$ cal/sq. cm/min. $=1.35\times 10^{6}$ ergs/sq. cm/sec. The sun has a magnitude of -26.72 and hence has the effect of $10^{27.72\times 0.4}$ or 1.22×10^{11} first magnitude stars. According to Seares,[4] starlight is equivalent to 1092 first mag. stars. Hence the intensity of starlight is $1092/4\pi$ first mag. stars per sq. radian. Call this I. Then the total energy E flowing per sq. cm into the top of the atmosphere in starlight is given by

$$E=I\int_0^{2\pi}d\phi\int_0^{\pi/2}\sin\theta\cos\theta\,d\theta=\pi I\therefore E=\frac{1092}{4}\times\frac{1.35\times 10^{6}}{1.22\times 10^{11}}=3.02\times 10^{-3}\text{ ergs}$$

i.e. the *total energy coming into the earth in the form of cosmic rays is very close to one-tenth the total energy of starlight.*

The whole of this cosmic-ray work has been done with the aid of funds provided by the Carnegie Corporation of New York and administered by the Carnegie Institution of Washington.

Norman Bridge Laboratory of Physics,
California Institute,
March 19, 1928.

[4] Seares, Astroph. Jour. **62**, 373 (1925).

FINE STRUCTURE IN THE *K*-SERIES OF COPPER AND NICKEL AND THE WIDTH OF SPECTRAL LINES

By Harris Purks

Abstract

Width and fine structure of the $K\alpha_1$, $K\alpha_2$ and $K\beta$ lines of Ni, Cu, Mo and Ag.—High resolving power was obtained by means of the double x-ray spectrometer. The minimum width of slits was 1.75 mm. Wide slits made possible the study of the lines after second order reflection from two calcite crystals. Ionization currents were measured with a Compton type electrometer of sensitivity 5000 mm per volt at one meter. At 40 kv and in the first order the widths at half-maximum of the lines (in X.U.) were found to be: Ni $K\alpha_{1,2}$, 0.66; Cu $K\alpha_{1,2}$, 0.63; Mo $K\alpha_{1,2}$, 0.47; Ag $K\alpha_{1,2}$, 0.43; Mo $K\beta_{1,2}$, 0.43; Ag $K\beta_{1,2}$, 0.40. In the second order the estimated width of the components of Ni $K\alpha_{1,2}$ and Cu $K\alpha_{1,2}$ was 0.4 X.U. which was also the estimated width of Ni $K\beta_{1,2}$ and of Cu $K\beta_{1,2}$. Structure to the lines of nickel and copper was clearly indicated by the shapes of the curves. The first order curves of the $K\alpha$ lines of Ni and Cu showed an asymmetry on the long wave-length side which was checked as regards position and intensity by the second order curves. It was found that the lack of symmetry could be explained by the presence of weak lines at displacements 0.42 and 0.35 X.U. from Cu $K\alpha_1$ and Cu $K\alpha_2$, respectively, and 0.45 and 0.38 X.U. from Ni $K\alpha_1$ and Ni $K\alpha_2$, respectively. The $K\beta$ doublets of Mo and Ag were clearly resolved after first order reflection from two crystals. Their separations were, for Ag $K\beta_2-K\beta_1$ 0.63 X.U. and for Mo $K\beta_2-K\beta_1$, 0.58 X.U. These doublets for Ni and Cu were not resolved after second order reflection. However, the shapes of the curves obtained permitted a solution of the problem of intensities and displacements. Their separations were 0.32 X.U. and 0.29 X.U. for Cu $K\beta_2-K\beta_1$ and Ni $K\beta_2-K\beta_1$, respectively. The shapes of the $K\beta$ curves of Ni and Cu showed evidence of the spark line $K\beta'$ and the curve of Cu showed evidence of a line corresponding to the $K\beta''$ line found by Hjalmer for Ca, K, Cl.

Variation with potential of the width of the $K\alpha$ lines of Ni, Cu, Mo and Ag.—Curves showing a variation of width of the $K\alpha$ lines with voltage were obtained. The widths increased with increasing voltage but seemed to approach a limiting value at about 40 kv. The width at the excitation potential was about two-thirds the width at 40 kv. The variation is explained as due to the successive appearance of spark lines.

BY A method proposed by Professor Bergen Davis it has been found possible to gain greater resolving power for x-rays by means of the double x-ray spectrometer. This method has been described in two recent papers by Davis and Purks.[1,2] Simultaneously, Ehrenberg and Mark[3] and Ehrenberg and Susick[4] have used the double x-ray spectrometer for the determination of the natural breadth of the spectral lines. These authors used only first-order reflection and made no use of the possibilities of very wide slits. In the first two papers mentioned[1,2] it has been shown that this method permits the use of wide slits which in turn permits the use of the

[1] B. Davis and H. Purks, Proc. Nat. Acad. Sci., **13**, No. 6, (June, 1927).
[2] B. Davis and H. Purks, Proc. Nat. Acad. Sci., **14**, No. 2, (Feb. 1928).
[3] Ehrenberg and Mark, Zeits. f. Physik. **42**, (May, 1927).

higher orders of reflection with considerable energy. It has been found possible[2] to obtain a rocking curve of Mo$K\alpha_1$ after third-order reflection from both crystals.

Apparatus and Method

Two split calcite crystals were mounted as shown in Fig. 1. The slits were 1.75 mm wide and 6 mm high except in the case of the second order curves of the K-lines of nickel. In this case the width was 2.75 mm. The distance between slits was 50 cm and the distance from the source of the x-rays to the center of the first crystal was about 80 cm. The distance between centers of crystals was about 5 cm. The ionization currents were measured by a Compton type electrometer of a sensitivity of 5000 mm per volt at one meter.

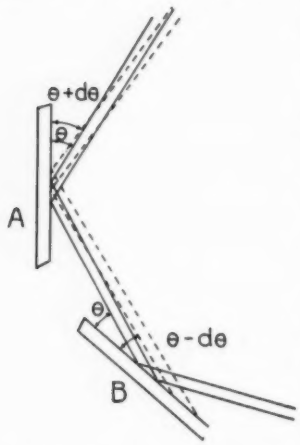

Fig. 1. Crystal arrangement.

In this method the first crystal A played the role of a collimator in that all the rays reflected from it were parallel to within the few seconds of arc given by the tolerance angle of the crystal. The wide slits permitted the reflection of a considerable range of wave lengths. Crystal B acted as an analyzer in that it selected from the number of bundles of parallel rays reflected from A that one which made with B the reflecting angle θ_n. This bundle alone was reflected from B.

From the geometry of the figure and the Bragg reflection law it follows that the angular displacement measured on crystal B between two wavelengths λ and $\lambda+d\lambda$ will be given by:

$$\Delta\theta=\frac{nd\lambda}{2d\cos\theta_n}+\frac{md\lambda}{2d\cos\theta_m}$$

where n and m are the orders of reflection from crystals A and B respectively.

The crystals were carefully adjusted as regards angles about a horizontal axis. The tube was placed so that the source and the center of the crystals formed a horizontal line. It was necessary to adjust the two crystals so that this line and the normals to the two crystals lie in the same plane. It was desirable that this plane be horizontal but small deviations from this condition were of no consequence since there was no collimation of the rays until they had struck the first crystal. The adjustment of the orientation of the crystals was done by finding the orientation of B about a horizontal axis which gave the minimum width to rocking curves. At this position the normals and the horizontal line lie in the same plane.

The width of rocking curves from crystal B are independent of the width of slits. This is obvious if the crystals are assumed perfect. A test was made and it was found that the widths of curves were independent of slit-width

as long as the beam did not strike the rough edges of the crystals. The maximum width which could be used was determined by the dimensions of the crystals and the angle of reflection. The only function of the horizontal width of slits was to confine the beam to the crystal path and to diminish the effects of scattered radiation.

The height of slits however does affect the width of curves. If crystal B is set at an angle $2\theta_n$ to crystal A then a horizontal ray of length λ will strike B at the angle θ_n. It will be reflected. Other rays of the same wave-length but not horizontal will be reflected from A and these rays strike B at an angle $(\theta_n - \epsilon)$. They are reflected from B only after it has been turned through the small angle ϵ. Such rays increase the widths of curves. They are eliminated by decreasing the height of slits. It was found that the widths of curves successively decreased with diminishing height of slits until a height of about 6 mm was reached. After this further diminution of height had no measureable effect upon the width of curves. Calculation shows that at this height the angle ϵ is approximately equal to the tolerance angle of the crystal, i.e., from four to six seconds of arc.

Relative intensities of lines measured by this method will be correct under certain conditions. In general crystal A is not rotated. The slits are made so wide that both lines are reflected at one setting. The curves from crystal A were about 15 minutes wide at half-maximum. These curves were flat to better than one percent over a region of four or five minutes. The intensities of two lines whose separation is not greater than the above interval may be compared by obtaining rocking curves from crystal B since the two lines are reflected in their true ratio of intensities from crystal A, when A is set at any position within the interval containing the flat top of the curve.

Results

The spectral lines closely investigated in the course of this experiment were the K-series of copper and nickel. In addition a few measurements were taken of the K-series of molybdenum and silver.

Ehrenberg and Mark[3] and Ehrenberg and Susick[4] have measured the widths of certain spectral lines by a similar method. Among their results are listed the half-widths of copper K-lines. The observations were made at first-order reflection. They corrected for the effect of the crystal itself upon the width of lines. Their correction formula was:

$$H_\lambda = (H_2^2 - H_1^2)^{1/2} 2d \cos\theta_n / 2n$$

where H_2 and H_1 are one-half the angular widths at half-maximum of rocking curves taken with crystals as in Fig. 1 and with parallel crystals respectively. The half-value is taken because the angular displacement measured on crystal B is twice the Bragg law differential for a single crystal. In addition they have divided again by two so that their results give the half-width at half-maximum.

[4] Ehrenberg and Susick, Zeits. f. Physik, **42**, (May, 1927).

In the course of this experiment it was found that when both crystals were set for first-order reflection of the Cu $K\alpha$ lines the curves were 44 seconds wide at half-maximum. This corresponded to a wave-length interval of 0.63X.U. An attempt was made to reduce the width of the curve by decreasing the height of slits below 6 mm. No decrease resulted. This width of 0.63X.U. for the total width checks well with the half-width of 0.35X.U. found by Ehrenberg and Susick.

The $K\alpha$ lines of nickel were also investigated. A width of 46 seconds was obtained which corresponds to a wave-length interval of 0.66X.U.

The curves obtained were not symmetrical. The slopes on the two sides were equal but in each case there appeared on the long wave-length side a bulge which had the appearance of a weak unresolved line. It was first thought that these bulges were due to crystal imperfections of some kind and an attempt was made to eliminate them by making the beam fall on different crystal reflecting areas. In each case however the same bulge appeared. In order to get an approximation for the position, width, and intensity of a weak line which would explain the asymmetry, the principal line was assumed to be symmetrical and its ordinates subtracted from the experimental curve. Typical curves are shown in Figs. 2 and 3.

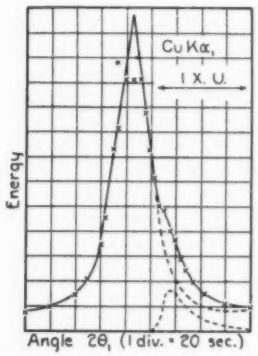

Fig. 2. Rocking curve—Cu $K\alpha_1$—first order.

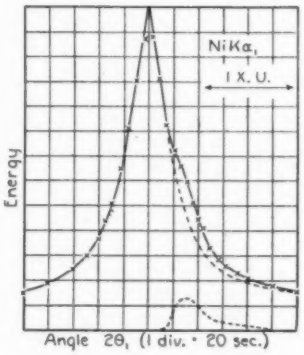

Fig. 3. Rocking curve—Ni $K\alpha_1$—first order.

By the subtraction of ordinates it was found that the bulges could be explained by weak lines at displacements of 0.42X.U. and 0.35X.U. to the long wave-length sides of Cu $K\alpha_1$ and Cu $K\alpha_2$ respectively, and 0.45X.U. and 0.38X.U. to the long wave-length sides of Ni $K\alpha_1$ and Ni $K\alpha_2$ respectively.

The $K\alpha$ lines of molybdenum have been investigated at first order by Davis and Purks.[1] They showed no asymmetry. In the course of this experiment the $K\alpha$ lines of silver were also investigated. At first order these lines showed no asymmetry. The widths of the $K\alpha$ lines of molybdenum and silver measured at first order were 32 seconds and 30 seconds respectively.

It was noticed that at lower voltages the curves of Cu $K\alpha$ were narrower than at high voltages. This led to the investigation of the

width-voltage relations. The results are shown in Fig. 4. The curves at voltages near the excitation voltage were about two-thirds the width at 35 kilovolts. The widths increased with voltage quite rapidly at first and then seemed to approach a limiting value. The widths of all lines investigated above 30 kilovolts could be determined with an accuracy of better than two percent. For voltages below 30 kilovolts the copper and nickel curves could be determined to at least 4 percent. The widths of the molybdenum and silver curves were not so precise near the excitation limit. This was due to the magnitude of the general radiation intensity in comparison to that of the lines and also to the difficulties of shielding for small reflecting angles. The precision of these latter widths near the limit was probably not better than 15 percent. Nevertheless the results did show a definite break in the widths and that this break was sharp in comparison to that for copper and nickel.

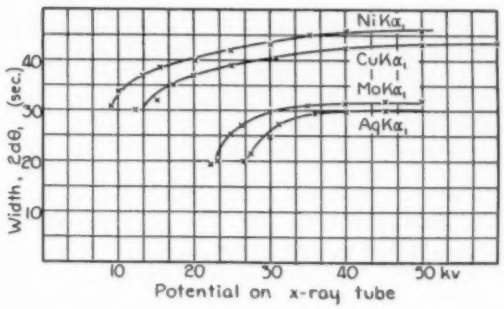

Fig. 4. Increase of width with voltage.

The $K\beta$ lines of the elements mentioned were also investigated at first order. The molybdenum and silver $K\beta$ doublets separated clearly. The separations were 0.58X.U. and 0.63X.U. for molybdenum[1] and silver respec-

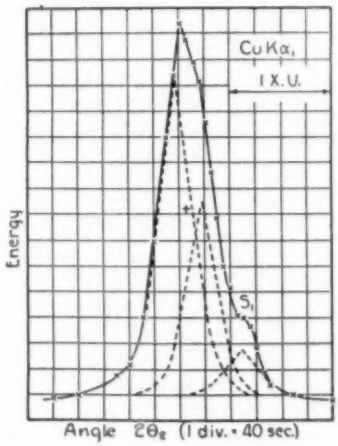

Fig. 5a. Cu $K\alpha_1$—second order.

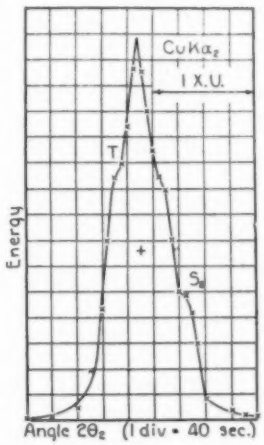

Fig. 5b. Cu $K\alpha_2$—second order.

tively. The $K\beta$ lines of copper and nickel were not resolved into doublets at first order but the curves showed indications of the presence of the doublet. The widths of the $K\beta$ lines of copper and nickel are not listed here because of their multiple nature. The widths of the $K\beta_1$ and $K\beta_2$ lines were found to be 30 seconds and 28 seconds for molybdenum and silver respectively.

It had been found[2] that when both crystals were set for second order reflection of Mo $K\alpha_1$ and Mo $K\alpha_2$ the curves were narrower than at first order. This could be explained in part by the smaller reflecting area of the crystals at second order. In an effort to resolve the weak lines indicated by the bulges on the $K\alpha$ lines of copper and nickel these lines were investigated at second-order reflection. Unlike the molybdenum lines these lines were almost twice as wide at second order as at first order. It was inferred that this was due to the natural width of the lines or a structure of some sort which spread out under the increased dispersion. The curves obtained are shown in Figs. 5 and 6. It will be noticed that in each case there is an asymmetry which corresponds in position and intensity to that found at first order. This asymmetry is lettered S on the curves. In addition to this there was noticed other asymmetrical bulges nearer the center of what at first order appeared to be one principal line.

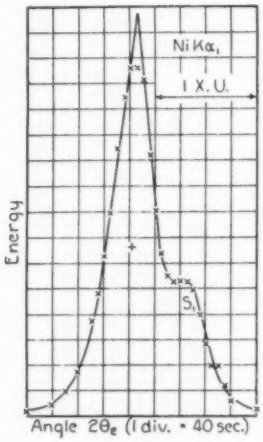

Fig. 6a. Ni $K\alpha_1$—second order.

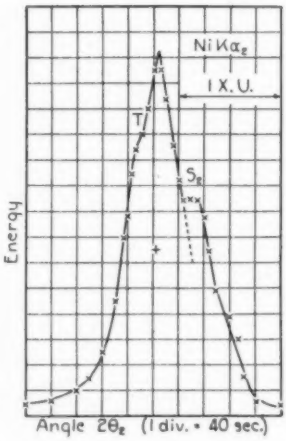

Fig. 6b. Ni $K\alpha_2$—second order.

The $K\beta$ doublets of copper and nickel were also investigated at second order. The resolution of the two components was not perfect but the curves (Figs. 7 and 8) permit quite definite conclusions as to their separation and intensities. Possible solutions to the curves are shown by the dotted lines. The copper doublet was more in evidence than the nickel doublet. The separation was not as great in the case of nickel and also the nickel components may be reasonably expected to be slightly wider. The observed β doublet separations are 0.32X.U. and 0.29X.U. for copper and nickel respectively. In addition to the doublet lines there appeared evidence of the spark lines $K\beta'$ and $K\beta''$ which have been found for some of the elements of lower atomic number. The $K\beta'$ lines on the long wave-length side were fairly definite but the $K\beta''$ lines were merely indicated by the slope of the short wave-length side of the main body of the curves. The $K\beta''$ lines have been found for only three elements Cl, K, Ca.[5]

[5] Hjalmar, Zeits. f. Physik **7**, 341–350 (1921).

Discussion

The second-order curves of the Cu $K\alpha$ and Ni $K\alpha$ lines (Figs. 5 and 6) indicate the existence of structure within the lines. Obviously any attempt to solve the problem of structure will lead to very uncertain conclusions. In the case of two unresolved lines calculations may be made which certainly lead to approximations. But when there are three or more components present many solutions are possible. A possible solution of the structure of Cu $K\alpha_1$ is shown by the dotted lines in Fig. 5(a). There may be present more than three components but if these others are assumed to be of weaker intensity then at least the width of the components given by the dotted lines is reasonable. The width thus found is 60 seconds at half-maximum or a wave-length interval of 0.4X.U.

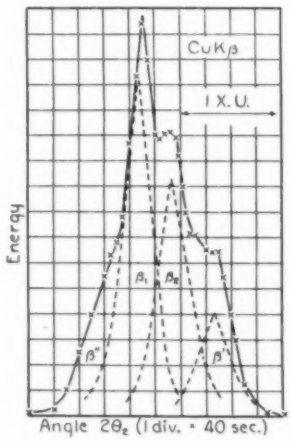

Fig. 7. Cu $K\beta$ doublet.

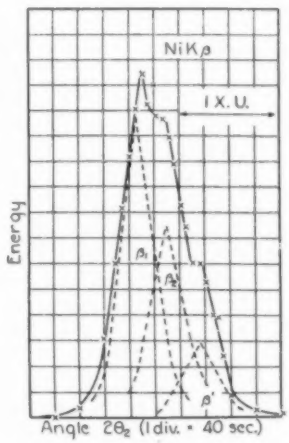

Fig. 8. Ni $K\beta$ doublet.

The significance of the width of the curves at half-maximum is small if as is indicated the lines have structure. For example, the curve of Ni $K\alpha_2$ (Fig. 6b) would have its width reduced from 125 seconds to about 90 seconds if the cause of the asymmetry at S had its intensity reduced by one-sixth of its value. This affords an explanation why the curve of Ni $K\alpha_1$ ($Z=28$) is narrower at half-maximum than that of Cu $K\alpha_1$ ($Z=29$).

The width of the component lines is of great importance. It has been found[6,7] that the natural breadth of a spectral line calculated on the basis of damped oscillations of an electron should be independent of the wave-length and of magnitude 0.12X.U. From the curves it is seen that a reasonable value of the widths of the components of the copper and nickel $K\alpha$ lines is 0.4X.U. It has been found[2] that the $K\alpha$ lines of molybdenum show evidence of components of width slightly less than 0.1X.U., which is less than the predicted value of 0.12X.U. These experiments indicate that the breadths of the components are not constant from element to element and

[6] G. E. M. Jauncey, Phys. Rev. Jan. 1922.
[7] A. H. Compton, X-rays and Electrons, p. 56.

that the breadth of what is called the emission line is dependent upon the number, width, position, and intensity of these components.

The work of Dauvillier, Hjalmar, Siegbahn, Dolejsek and others shows that the K-series of the elements of lower atomic numbers contain many lines not predicted by the regular energy level diagram. These lines have been referred to as spark lines and are explained by Wentzel as due to multiple ionization of the inner levels of the atom. The lines found by these authors appear (with one exception $K\beta'$) on the short wave-length side of the principal lines. The spark lines found by Dauvillier[8] associated with the $K\alpha$ lines were at a displacement corresponding to the order of 100 volts. The lines associated with the $K\beta$ lines had a displacement corresponding to less than 10 volts. Siegbahn and Larsson[9] have found that the $L\alpha$ lines of molybdenum are complex. These lines have associated with them spark lines whose displacement corresponds to about 10 volts.

The lines in the neighborhood of the $K\alpha$ lines of nickel and copper found in the course of this experiment all lie (with the exception of the line indicated by the asymmetry at T, Figs. 5 and 6) on the long wave-length side of the principal lines. The magnitude of their displacements corresponds to about 3 volts. Since the $K\alpha$ lines follow from the transition ($L \rightarrow K$) the suggestion is offered that these spark lines follow from transitions from multiply ionized L-levels to normal K-levels. The energy differences and the directions of displacements are consistant with this suggestion.

The curves of Siegbahn and Larsson show that as the voltage increased there appeared more spark lines in the neighborhood of Mo $L\alpha$. This caused a marked increase in the width of the line. The curves of Fig. 4 indicate that the widths of the $K\alpha$ lines of the elements investigated increased with voltage. These curves are consistent with the theory of successive appearance of spark lines as the voltage increased. An attempt was made to obtain width-voltage curves with both crystals at second order, but at voltages near the excitation limit the available energy was not sufficient to give accurate curves.

A table of the results of this experiment is given below. No attempt has been made completely to solve the problem of structure of the $K\alpha$ lines. However, the components indicated by the bulges found at first order are listed because the results at second order confirm them (see the bulges marked S, Figs. 5 and 6). These displacements of S on the second order curves check very well those found at first order provided the displacements be measured from the middle of the main curve at half-maximum rather than from the peak. These middle points are designated by the crosses (+) on Figs. 5 and 6.

These displacements of S from the center of the principal lines are significant in that they represent an interval in which there is evidence of structure. The maximum interval in which there is structure is larger than this by perhaps fifty percent.

[8] A. Dauvillier, Jour. d. Physique, Serie 6, **3**, (July, 1922).

[9] Siegbahn and Larsson, Ark. o. Physik, **18**, No. 18, (1924).

The widths of lines listed are not corrected for crystal imperfections by the Ehrenberg and Mark formula. This was considered unnecessary since the correction factor $(H_2^2-H_1^2)^{1/2}$ is equal practically to H_2 since

TABLE I. *Values for the widths, and separations of the components, of K series lines of Ni, Cu, Mo and Ag (40 kv.).*

Lines	Total Width Seconds	X. U.	Lines	Displacements Seconds	X. U.
		First Order			
Ni $K\alpha_{1,2}$	46	0.66	Ag $K\beta_2-K\beta_1$		0.63
Cu $K\alpha_{1,2}$	44	.63	Mo $K\beta_2-K\beta_1$		.58
Mo $K\alpha_{1,2}$	32	.47	S_1-Cu $K\alpha_1$		.42
Ag $K\alpha_{1,2}$	30	.43	S_2-Cu $K\alpha_2$		.35
Mo $K\beta_{1,2}$	30	.43	S_1-Ni $K\alpha_1$		.45
Ag $K\beta_{1,2}$	28	.40	S_2-Ni $K\alpha_2$		.38
		Second Order			
Components of			S_1-Cu $K\alpha_1$	80	0.5
Ni $K\alpha_{1,2}$ and			S_2-Cu $K\alpha_2$	65	.4
Cu $K\alpha_{1,2}$	60	0.4	S_1-Ni $K\alpha_1$	80	.5
Ni $K\beta_{1,2}$	60	.4	S_2-Ni $K\alpha_2$	65	.4
Cu $K\beta_{1,2}$	60	.4	Cu $K\beta_2-K\beta_1$	50	.32
			Cu $K\beta'-K\beta_1$	100	.7
			Ni $K\beta_2-K\beta_1$	45	.29
			Ni $K\beta'-K\beta_1$	100	.7

the value of H_1 found in these laboratories was less than two seconds of arc at second order and about three seconds of arc at first order.

In conclusion the author wishes to express thanks to Professor Bergen Davis for many helpful suggestions and for the use of the double x-ray spectrometer devoted to his personal researches.

PHYSICS LABORATORIES,
COLUMBIA UNIVERSITY,
March 12, 1928.

AN ATTEMPT TO ADD AN ELECTRON TO THE NUCLEUS OF AN ATOM

By William D. Harkins and Webster B. Kay

Abstract

Since the present theories of the atom indicate that an electron is attracted by the atom nucleus, they also suggest that the principal difficulty in accomplishing the addition of an electron is in obtaining such (unknown) conditions as make the attraction effective. Electrons with a velocity corresponding to 138,000 to 145,000 volts were caused to strike the surface of liquid mercury. The mercury served as an anti-cathode in an x-ray tube. (This work was done before the electron tube of Coolidge was available.) When the experiments were begun it was not expected that positive results would be attained, since either the voltage may be too low, or the number of electrons shot into the surface (4×10^{21}) too small, but it was thought to be of value to show this to be true. The addition of an electron to the nucleus of an atom of mercury should give an atom of gold. Since no gold was found in the exceedingly sensitive tests used, it is shown that either less than one in a billion of the electrons attached itself to an atom nucleus, or else all or a part of the nuclei produced were not sufficiently stable to endure for the period (24 to 48 hours) of the tests.

1. Introduction

THE nucleus of an atom is supposed to have a net positive charge equal (in electron units) to the atomic number (Z) of the element. It has been found that an alpha-particle with a net positive charge of $2e$ may attach itself to the nucleus of an atom of nitrogen provided its velocity immediately before impact is about 1.8×10^{9} cm per second (or about 7×10^{6} electron equivalent volts of energy). One photograph obtained by Harkins and Shadduck indicates that such an attachment may occur at a velocity as low as 1.57×10^{9} cm per second (5.1×10^{6} electron volts).

The scattering of alpha-particles by gold indicates that the inverse square law holds at distances between the centers of the nucleus of the gold atoms and that of the alpha-particle greater than 3.2×10^{-12} cm. Since the magnitude of the net positive charge of the nucleus of an atom of mercury is almost the same as that of gold, it may be considered that the above value is as valid for mercury as for gold. Now, if the inverse square law holds for electrons also at distances of nuclear approach greater than 3.2×10^{-12} cm an electron should gain a velocity of about 0.991 c (2.9×10^{10} cm/sec.) if it falls from rest outside the atom to a distance of 3.2×10^{-12} cm from the nucleus of the atom. This corresponds to the velocity given to an electron by a potential fall of three million volts.

Thus it seems that the electron should, provided it attains a condition such that the net attractive effect of the nucleus becomes available, approach the nucleus of the atom of mercury with about 20 times the velocity and more than one-half the kinetic energy of an alpha-particle which attaches itself to the nucleus of a light atom.

If the above point of view is accepted, an interesting conclusion emerges. By present methods it is not possible to accelerate electrons by potentials greater than about 300,000 volts, except by the use of several Coolidge electron tubes in series. Such a potential is very small compared with the potential drop in the atom itself. Thus the use of the external electric field for the acceleration of electrons is needed only to drive the electron into the atom with sufficient (possibly critical) velocity and energy so that the attractive force between the nucleus and the electron may be effective. The magnitude of the energy essential for this purpose is unknown, but it may not be unreasonable to suppose that it is greater than that necessary to excite the hardest x-rays which the substance emits.

2. Attempt to Add an Electron to the Nucleus of an Atom of Mercury

In the experiments reported in the present paper a mercury surface was bombarded by electrons with an energy of 145,000 volts, which corresponds to a velocity of 1.9×10^9 cm/sec. While this voltage is much greater than that required to excite the hardest x-rays of mercury, it was the opinion of the writers that a much higher voltage would give a considerably greater chance of success in the addition of an electron to the nucleus of the mercury atom, but the voltage used was at the time the highest available for this work. On this account it was our wish to use an element of considerably lower atomic number. However, mercury[1] was selected for the work because (1) it may be separated almost entirely from the next lower element (gold), and (2) an exceedingly small amount of gold (10^{-9}g) may be detected in a comparatively large amount of mercury (130g). It happened that we also possessed a considerable amount of mercury which is not only free from detectable amounts of gold, but is also considerably lighter than ordinary mercury (about 0.1 unit). Now Aston had reported the presence in mercury of an isotope isobaric with gold (atomic weight = 197). If this had been correct, our sample, produced by Harkins, Mulliken and Mortimer, would have been richer with respect to this isotope than any other known sample of mercury.

Later Aston found this observation to be erroneous, so the chance of producing gold would seem to be best with the mercury isotope of mass

[1] We were especially desirous of avoiding the use of mercury on account of the considerable notoriety attached to the finding of gold in mercury arc lamps by Meithe and Stammreich, (Miethe and Stammreich, Naturwissenschaften **12,** 597, 744, 1211 (1924), **13,** 635 (1925); Zeits. f. Anorg. Chem., **140,** 368 (1924); **148,** 93 **149,** 263 (1925); **150,** 350 (1926); Phys. Zeits. **26,** 842 (1925)) and the idea that it was obtained by a transmutation of some of the mercury. In this work the total applied potential was only 220 volts, and the effective velocity of the electrons ejected corresponds to only a small fraction of the potential. Miethe's method has been tested by a number of investigators, (Haber, Jaenicke and Matthias, Zeits. f. Anorg. Chem. **513,** 153 (1926); Piutti and Boggio-Lera, Giornale de Chemica industriale **8,** 59. Rend. R. Accad. Napoli (S) **31,** 194 (1926); Riesenfeld and Haase, Ber. der Deut. Chem. Ges., **59,** 1625 (1926); Tiede, Schleede, Goldschmidt—ibid. 1629; Sheldon, Estey, and Maily, Scientific American, 1925, p. 291), all of whom found that no gold was produced. Notices of the results of our own work were published two years ago (Metallbörse **16,** 1117 (May 19, 1926), report of the results of the work of the writers) without our knowledge.

number 199. It is not unlikely, even if gold happened to be formed in our experiments, that the gold atoms produced were not sufficiently stable to exist until the chemical test was completed.

The only work on mercury in which a high total potential was used is that of Nagoaka.[2] He obtained a high potential discharge from an induction coil between a metal point in oil and a mercury surface. The velocity of the electrons which struck the surface of the mercury was not determined, but was probably only of the order of a few hundred or a few thousand volts, since the discharge was produced in oil at atmospheric pressure. However, Nagoaka found gold in the mercury after this treatment.

General method and the stability of atom nuclei produced. The general method used in this work was to accelerate the electrons from a Coolidge cathode in an x-ray tube in which 9 cc of mercury was used as an anticathode. The potential on the tube was 138,000 to 145,000 volts. The mercury was tested for gold after enough current had been passed to form 1.5 g of gold provided each electron should attach itself to the nucleus of a mercury atom. Since the limit of detection was about a billionth of a gram of gold, or slightly less, it was necessary for the detection of this element that the yield should be more than one trillion of its atoms, with a sufficient stability to have a life of from 24 to 48 hours, that is, the period of the test.

Apparatus and method. The method employed to bombard the mercury atoms with electrons involved the use of the mercury as a target for cathode rays of high velocity. This amounted to an x-ray tube with a mercury anticathode. Such a tube involves considerable change in the design of the anticathode on account of the high vapor pressure of mercury, which is 0.0004 millimeter at 0°C. Since the vacuum necessary for the successful operation of the tube is of the order of 10^{-6} millimeter pressure, it is evident that even at 0°C this vapor pressure is much too great. This difficulty is increased by the fact that the heating effect at the anticathode by the cathode rays makes the vapor pressure still greater. It is obvious, therefore, that the mercury must be kept at a temperature considerably below 0°C. Extrapolation of the empirical equation for the vapor pressure of mercury showed that at about −30°C its vapor pressure would be sufficiently low. Of the various cooling agents available with which to obtain a temperature in this neighborhood, liquid ammonia was the only low boiling liquid available in sufficient quantities.

The construction of the tube is shown in Fig. 1. The principal parts are the discharge chamber *A*, the cathode *B*, and the anticathode *C*. The discharge chamber is made from a one liter round bottom Pyrex flask. The Coolidge cathode is a medium focus spiral filament of tungsten which is heated by a 6 volt storage battery. The anticathode resembles an inverted Dewar bottle with the outer jacket fused to the bottom of the flask. A shallow cup in which the mercury is held is made in the end of the inner

[2] Nagoaka, Naturwiss, **13**, 684 (1925), **14**, 85 (1926), Nature **116**, 95 (1925). J. de phys. et de Radium **6**, 209 (1925); Soc. Franc. de Phys., Rev. gén. des Sciences pure et appl. **36**, 59 (1925).

tube. Through the bottom of this cup is sealed a tungsten wire which is fused into the end of a small tube. An outside electrical connection with the mercury is then made through this small tube by a copper wire in contact with the tungsten wire. The bottom is closed with a tight fitting rubber stopper through which pass the inlet and outlet tubes for the liquid ammonia. The outlet tube extends almost to the top of the inner tube so that the mercury cup is always surrounded by the liquid. To make the stopper leak proof and more rigid, it is covered with sealing wax.

The liquid ammonia is pumped from the Dewar bottle *D* to the anticathode and back again by a small iron gear pump (*E*) which is driven by an electric motor. As the liquid evaporates the vapors escape through the tube at the top of the bottle. The temperature of the ammonia may be lowered below the boiling point by pumping off this vapor.

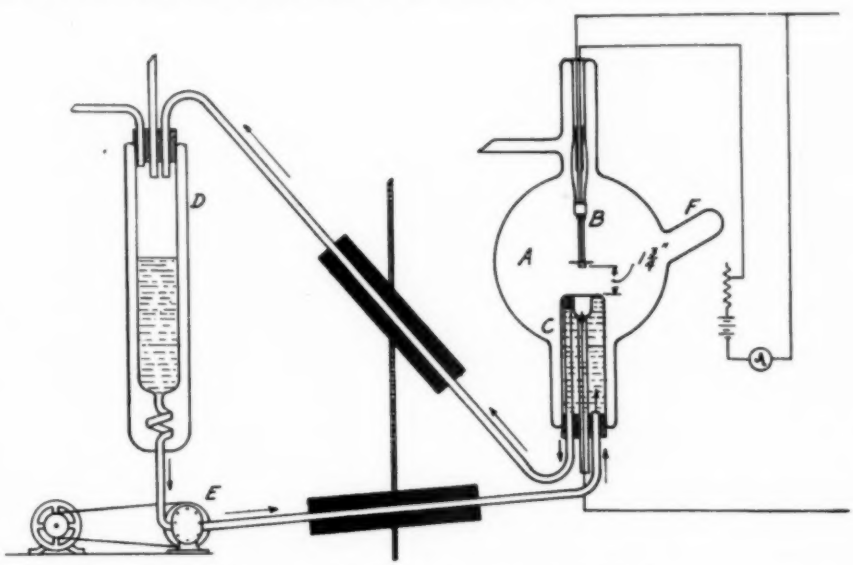

Fig. 1. X-ray tube with a mercury anticathode.

Electron bombardment of the mercury. A nine cubic centimeter sample of the pure mercury was introduced into the mercury cup of the anticathode through the side arm *F*, which was then sealed off. The tube was evacuated by a set of two mercury vapor condensation pumps backed by a vacuum oil pump. The pressure was measured by a MacLeod gage. Mercury vapor was condensed in a liquid air trap and thus prevented from entering the tube while it was in operation. The tube was excited by an x-ray transformer of the closed magnetic-circuit type and the potential across the secondary was measured by a sphere gap connected in parallel with the tube.

Two experiments were performed. In the first the tube was operated at 112,000 volts and about 1.5 milliamperes for a total of 37 hours. In a second experiment it was operated at 138,000 volts and about 2 milliamperes for 81 hours and 146,000 volts and 2 milliamperes for 4 hours. The mercury was tested after each experiment and no trace of gold could be found.

Discussion. From the number of coulombs of electricity passed through the tube, the first experiment should have yielded 0.4 gram of gold and the second 1.42 grams if every electron had lodged in the nucleus of a mercury atom. Since the sensitiveness of the analytical method was one billionth of a gram of gold, it is evident that less than one electron in a billion was effective. Such a result may be explained in several ways. It is possible that the percentage of electrons that lodge in the nucleus is many times smaller than one in a billion and, therefore, the experiments were not conducted for long enough time. Also, as discussed in the introduction, even if an electron added itself to the nucleus the resulting atom may be unstable and, therefore, could not be detected by chemical methods. However, it seems that the failure of these experiments may possibly be due to too low a potential togive the electron sufficient speed to drive it sufficiently close to the nucleus.

Test for Gold. In the experiments here described, particular care was taken to be sure that the original mercury did not contain gold. The mercury used was a 17 cc sample produced in this laboratory by Harkins and Mortimer[3] in their work on the separation of the isotopes of mercury. It had been slowly vaporized in a high vacuum and the vapors diffused through filter paper at least nine times. Previous to this treatment it had been washed in the usual way with a dilute solution of nitric acid and mercurous nitrate and distilled three times at low pressure. Only the middle portion of the distillate was retained each time. No gold was found when this sample was tested, which indicates that if any were present its amount was probably less than four parts in a trillion parts of mercury.

The method of analysis was a modification of a micro-fire assay method employed by Haber[4] in the quantitative estimation of gold from the water of the Rhine River. It consisted, essentially, in the collection of the gold in lead, the cupellation of the lead, and the measurement of the gold bead under a high power microscope. It was carried out as follows. The sample of mercury was distilled slowly in an apparatus of convenient size at a pressure of 0.01 mm and a temperature of 90°C. The rate of distillation was one cc in 43 minutes. When about three grams remained in the distilling flask the distillation was stopped and this residue transferred to an alundum filter crucible and dissolved in dilute nitric acid which contained neither halogens nor noble metals. After the crucible was washed with water until free from mercurous salts, it was dried and 0.5 gram each of pure lead and lead oxide together with 0.2 gram of boric acid were added and the scorification started over a small gas flame. However, the process should not be carried to completion in the alundum crucible because of the difficulty encountered later when the small lead bead has to be removed from the bottom of the crucible in preparation for the cupellation. Therefore, after the molten lead had been allowed to come in contact thoroughly with the inside of the crucible, the flame was removed and the lead button transferred to a porcelain crucible. One-half gram of lead oxide and 0.2 gram of boric

[3] Unpublished work.

[4] Haber and Jaenicke, Zeits. anorg. Chem. **146**, 156 (1925).

acid were again added and the scorification continued until the button was about a millimeter in diameter. It was then removed and cupelled in a shallow, unglazed porcelain dish with a thin bottom. This dish was so thin that its contents could be examined under a microscope with transmitted light. Since the porcelain did not act as an absorbent, the gold bead remained behind in an envelope of slag. The diameter of the bead was measured with a microscope by the use of a filar micrometer eyepiece.

The porcelain dish used as a cupel was made from a small crucible cover. The handle of the cover was removed and the top ground on a glass plate with emery until it was about one millimeter thick. The glazed surface was removed by the use of a few drops of concentrated hydrofluoric acid.

The reagents, lead, lead oxide and boric acid used in the analysis were especially prepared and purified in order to be certain that they contained no gold. The lead was prepared from Kahlbaum's lead acetate.

The solution of the acetate was freed from any trace of noble metals by warming with thio-acetic acid until 10 grams of the lead from such lead acetate gave no visible sign of a residue on cupellation. The crystallized acetate was then ignited to lead in a covered crucible over a blast lamp. A portion of this lead was dissolved in pure nitric acid and the resulting lead nitrate crystallized twice. It was then heated on an electric hot plate until it decomposed into lead oxide. The boric acid was purified by twice crystallizing Kahlbaum's purest boric acid from hot water. Tests for gold were made on these reagents using lots several times greater than were employed in testing the mercury which had been bombarded by electrons.

UNIVERSITY OF CHICAGO,
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MULTIPLET SEPARATIONS FOR EQUIVALENT ELECTRONS AND THE ROENTGEN DOUBLET LAW

By S. Goudsmit

Abstract

Expressions are derived for the separation of multiplets arising from configurations of equivalent electrons. It is explained why the Roentgen doublets obey the Sommerfeld formula, although this formula was derived formerly for a single electron only. The separations of more complicated multiplets are proved to be connected also with the Sommerfeld formula. According to Landé the multiplet separations can be characterized by factors, designated by Γ, which give the displacement of each level from the centre of gravity of the whole multiple level. The properties of these Γ factors are studied in this paper. They are quite analogous to the well-known properties of the magnetic separation factors, g, introduced by Landé for the explanation of the Zeeman effect. It is pointed out that there is a Γ sum rule, corresponding to the well-known g sum rule, stating that, for given quantum numbers of the electrons, the sum of the Γ values belonging to a certain total moment j is a constant, independent of the type of coupling of the electrons. This rule is important especially because it makes it possible to obtain expressions for the multiplet separations in general cases.

IN HIS celebrated paper on the building up of electron groups, Pauli[1] has shown that the absence of a given number of electrons from an otherwise complete configuration gives rise to quantum states analogous to those which appear when only this same number of electrons is present. Pauli has developed a rule for the determination of the quantum states and quantum numbers of an electronic configuration from those of the electrons involved in the configuration, but it gives us no information as to the energy relationships of these quantum states. It is well known that a single valence electron yields a doublet spectrum, and, according to Pauli's reasoning, the energy levels in the Roentgen spectrum, in the production of which one electron is absent from a complete group, should exhibit a similar structure. It has never been clearly explained however why the doublets in the Roentgen spectra are similar in their energy relationships to optical doublets due to single electrons, and follow exactly the same doublet formula, which up to now has been derived only for a single electron.[2]

Proof of the validity of the Roentgen doublet formula will be given in the present paper and still other properties of multiplet separations for a given number of equivalent electrons will be deduced. Results are given first for cases in which the spectrum shows normal multiplets.

For a single electron the doublet separation is given by the well-known Sommerfeld formula:

[1] W. Pauli, Zeits. f. Physik **31**, 765 (1925).

[2] W. Heisenberg and P. Jordan, Zeits. f. Physik **37**, 263 (1926).

$$\Delta\nu = \frac{R\alpha^2 Z_{eff}^4}{n^3 l(l+1)}$$

or for penetrating orbits, according to Landé, approximately:[3]

$$\Delta\nu = \frac{R\alpha^2 Z_i^2 Z_a^2}{n_a^3 l(l+1)}$$

(In these formulas R stands for the Rydberg constant, α the Sommerfeld fine-structure constant, n the principal quantum number, n_a the so-called effective principal quantum number, l the azimuthal quantum number in the notation of the new quantum mechanics, Z_a the effective nuclear charge in the outer part of the orbit, and Z_i that in the inner part).

In connection with what follows this formula for the doublet separation is written:

$$\Delta\nu = a(l+\tfrac{1}{2})$$

in which the factor a is consequently given by:

$$a = \frac{R\alpha^2 Z_{eff}^4}{n^3 l(l+\frac{1}{2})(l+1)}, \tag{1a}$$

or for penetrating orbits:

$$a = \frac{R\alpha^2 Z_i^2 Z_a^2}{n_a^3 l(l+\frac{1}{2})(l+1)} \tag{1b}$$

Table I gives the values of the total multiplet separations for equivalent p and d electrons, expressed in terms of the factor a associated with one single electron. The quantum numbers of the single electron must always be introduced in the expression for this factor a, independently of those of the multiplet given by the configuration. In the case of p electrons for example, l is accordingly always made equal to 1 in the factor a, while in the case of d electrons l is always made equal to 2.

The last column gives the value of the interval factor A. The meaning of this factor, which is constant for a given multiplet, may be understood by looking ahead to the expression for the interval rule given by Eq. (4). It will be seen that A is equal to the displacement divided by the number given by the interval rule. It may also be found by the same formula by dividing the separation of two adjacent levels by the larger of the inner quantum numbers belonging respectively to these two levels.

A minus sign before the separation indicates that it is an inverted multiplet, that is that the level with the largest total impulse moment j lies lowest. As would be expected the values in this table are correct only to an approximation as close, let us say, as the interval rule of Landé, for example.

[3] A. Landé, Zeits. f. Physik **25**, 46 (1925).

TABLE I. *Values of the total multiplet separations for the equivalent p and d electrons.*

Configuration	Multiplet	Total separation	Separation factor A	Configuration	Configuration	Multiplet	Total separation	Separation factor A	Configuration
p	^2P	$3a_i/2$	a_i	$-p^5$	d^3	$^2F'$	$-7a_i/12$	$-a_i/6$	$-d^7$
p^2	$^3P'$	$3a_i/2$	$a_i/2$	$-p^4$		^2D	$5a_i/6$	$a_i/3$	
p^3	$^2D'$	0	0	$-p^3$		^2D			
	^2P	0	0			$^2P'$	a_i	$a_i/3$	
					d^4	^5D	$5a_i/12$	$a_i/4$	$-d^6$
d	^2D	$5a_i/2$	a_i	$-d^9$		$^3H'$	$11a_i/10$	$a_i/10$	
d^2	$^3F'$	$7a_i/2$	$a_i/2$	$-d^8$		^3G	$27a_i/20$	$3a_i/20$	
	$^3P'$	$3a_i/2$	$a_i/2$			$^3F'$	$7a_i/12$	$a_i/12$	
d^3	$^4F'$	$7a_i/2$	$a_i/3$	$-d^7$		$^3F'$			
	$^4P'$	$4a_i/10$	$a_i/3$			^3D	$-5a_i/12$	$-a_i/12$	
	$^2H'$	$11a_i/10$	$a_i/5$			$^3P'$	$3a_i/2$	$a_i/2$	
	^2G	$27a_i/20$	$3a_i/10$			$^3P'$			
					d^5	all	0	0	$-d^5$

EXAMPLES

The spark spectrum of titanium[4] is the only spectrum in which an interesting group of levels arising from equivalent electrons is almost completely known. In the other spectra only one or two of the many expected multiplets have been found. In the case of the d^3 configuration in Ti II one of the two expected ^2D levels is still unknown. In this example however, the interval rule does not hold at all for the ^4P state, and it is of course impossible to decide whether it is valid or not for the doublets. Table II gives the

TABLE II. *Observed and calculated multiplet separations in Ti II.*

Term notation (Russell)	Ti II d^3 configurations Multiplet separations					
b^4F'	obs.	128.37	103.41	75.84		
	calc.	*133.2*	*103.6*	*74.1*		
a^4P'				122.29	32.05	
				74.1	*44.4*	
a^2H'	97.82					
	(*97.8*)					
a^2G		120.46				
		120.0				
b^2F'			−59.89			
			−51.8			
b^2D				129.38		
$-^2D$				—		
				Σ*74.1*		
a^2P'					125.02	
					88.9	
	$j=11/2$	9/2	7/2	5/2	3/2	1/2

observed and calculated multiplet separations, the latter being given in italics. The constant a_i was taken from the ^2H separation. The agreement is very good in most cases. Note especially the inverted ^2F term. It is very

[4] H. N. Russell, Astrophys. J. **66**, 283 (1927).

probable that the poor agreement for the separations between the levels with low values of j is due to the large deviations from the ordinary interval rule.

Another way to illustrate the formulas given here is to show that the constant a_i for different elements is represented by Eq. (1). Substituting Eq. (1) in Table I for the cases of equivalent d electrons, one finds that the total separation of the D level of highest multiplicity [if there is one] is just given by the well-known relativistic doublet law of Sommerfeld:

$$\Delta\nu = \frac{R\alpha^2(Z-\sigma)^4}{n^3l(l+1)}.$$

In the cases d^2, d^3, d^7 and d^8 one finds that 5/7 of the total separation of the F term of highest multiplicity occurring obeys the same formula. For the D separation this has actually been found independently from the observed data by Dr. O. Laporte.[5] The fact that he communicated these results to me gave rise to this investigation. It could also easily be shown that the formula also holds for 5/7 of the total F separations. Table III gives the total

TABLE III. *Total separations for the elements in the scandium row.*

Element	Configuration	Multiplet	Total separation	a_i	Screening constants
21 Sc	d	^2D	168.5	67	12.72
22 Ti	d^2	$^3F''$	386.7	111	12.64
23 V	d^3	$^4F'$	552.7	158	12.76
24 Cr	d^4	^5D	557.0	223	12.94
25 Mn	d^5	^6S	—	—	—
26 Fe	d^6	^5D	−978.1	−391	13.16
27 Co	d^7	$^4F'$	−1809.3	−517	13.24
28 Ni	d^8	$^3F'$	−2216.5	−632	13.53
29 Cu	d^9	^2D	−2042.9	−817	13.57
30 Zn	d^{10}	^1S	—	—	—

Roentgen doublet $M_{33}-M_{32}$, d^9 ^2D:13.0

separations of those terms in the scandium row of the periodic table. The constant a_i is calculated and also the screening constant σ by applying the relativistic doublet formula for non-penetrating orbits. Of course this will be only an approximation, but nevertheless σ appears to be near to the screening constant of the corresponding Roentgen doublet M_{33}-M_{32}.

THE Γ FACTORS

The multiplet separations are due to the interaction between the spin and the orbital motion of the electrons. In the case of a single electron this interaction energy is given by:*

$$\gamma_i = a_i l_i s_i \cos(l_i s_i) \qquad (2a)$$

* In this expression and in those which follow we indicate by a subscript i those quantities which belong only to a single electron.

[5] O. Laporte, Zeits. f. Physik **47**, 761, (1928).

We denote this expression by γ_i because it differs by only a factor from the γ factors introduced earlier by Landé.[6] In the case of several electrons it is permissible in general to neglect the interaction energy between the spin of one electron and the orbital magnetic field of another in comparison with the interaction with its own orbital field, as a first approximation.[7] The total interaction energy for several electrons is therefore:

$$\Gamma=\Sigma\gamma_i=\Sigma a_i l_i s_i \overline{\cos(l_i s_i)} \tag{2}$$

In general the angle between each s_i and its corresponding l_i is now no longer constant, and consequently the mean value of the cosine of the angle between the two must be introduced. In the case of normal multiplets it is known that all values of s_i combine to yield one resultant s, and likewise all values of l_i combine independently to form one resultant l. In this case it is easily shown that the mean cosine between each s_i and its corresponding l_i may be written:

$$\overline{\cos(s_i l_i)}=\overline{\cos(s_i s)}\cos(sl)\,\overline{\cos(l_i l)}.$$

Substituting in Eq. (2) we obtain for the total interaction energy:

$$\Gamma=ls\cos(ls)\Sigma a_i(s_i/s)\,\overline{\cos(s_i s)}(l_i/l)\,\overline{\cos(l_i l)}=Als\cos(ls). \tag{3}$$

If the value of $ls\cos(ls)$ for a particular multiplet is substituted in this formula, we obtain:**

$$\Gamma=Als\cos(ls)=\tfrac{1}{2}A\left[j(j+1)-l(l+1)-s(s+1)\right] \tag{4}$$

The symbol j indicates the resultant of s and l as defined above. It is therefore the total impulse moment of the atom in the given state; Eq. (4) obviously gives us also the well-known interval rule of Landé. In his treatment of the Paschen-Back effect, Landé[8] has investigated the relationships which connect these Γ factors for multiplets in a weak magnetic field with their values in a strong magnetic field, without being able however to make a study of their deeper significance at that time. He found that these Γ factors obey laws similar to those governing the behavior of the magnetic separation factors, denoted by g, which have been investigated in this connection by Pauli.[9] In the celebrated article on the building up of electron groups, referred to above, Pauli has also studied the building up of the g values of an atom from those of the individual electrons. We will now give our attention to a similar investigation of the Γ values, in order to obtain in this manner the results given above.

We must however first call attention to an interesting study by Slater,[10]

** First determined half empirically by Landé and later verified by new mechanics.

[6] A. Landé, Zeits. f. Physik **19**, 112 (1923).

[7] For the interesting case of the helium triplet in which these terms must be considered, see W. Heisenberg, Zeits. f. Physik **39**, 499 (1926).

[8] A. Landé, Zeits. f. Physik **19**, 112 (1923).

[9] W. Pauli, Zeits. f. Physik **16**, 155 (1923).

[10] J. C. Slater, Phys. Rev. **28**, 291 (1926).

who has attacked this problem from the same standpoint. Slater attempted to determine the values of the cosines in Eq. (3) with the aid of the vector model of the atom. We are of the opinion however that his results are not sufficiently conclusive. For instance he assumes that the cosine between every s_i and the resultant s of all values of s_i is always equal to $+1$ or -1. It is known however that when two quantum vectors are parallel in our nomenclature, it is not at all assured that the cosine as given by the new quantum mechanics must be $+1$ or -1. In fact this is almost always not the case. His results are consequently not entirely trustworthy, and valid in part only for large quantum numbers.

The Significance of the Γ Factors in the Spectrum

We will now investigate what part the Γ factors play in the structure of a spectrum. In a doublet level the two states are separated by just the difference between their Γ values, if no external field is present. If then Γ were equal to zero, the two doublet levels would fall together. Consequently the Γ values give the displacement of the actual levels from a hypothetical level, which would be realized if the interaction energy between the spin of each electron and its orbital magnetic field were neglected.

Furthermore in the case of any normal multiplet other than a doublet, the energies of the different levels differ only by their Γ values, since only the angle between the resultant s and the resultant l is changed. Therefore when we consider the group of levels belonging to a given multiplet, a particular value of Γ gives the displacement of the corresponding level from a certain hypothetical level, which, as may be easily shown by the interval rule of Landé as given in Eq. (4) above, lies exactly at the centre of gravity of the multiplet.

The Γ values of the different levels of a given multiplet may also be calculated with the aid of Eq. (4), in terms of A (which is the only unknown) if Γ is known for one of the levels. A little farther on we will show how Γ can be determined in certain cases for one of the levels of a multiplet. Two examples will illustrate the use of this formula. For a ^3P state, where $s=1, l=1, j=2, 1, 0$,

$$^3P_2,\ \Gamma=+A\quad ^3P_1,\ \Gamma=-A\quad ^3P_0,\ \Gamma=-2A.$$

For a ^4F state, where $s=1\frac{1}{2}$, $l=3$, and $j=4\frac{1}{2}$, $3\frac{1}{2}$, $2\frac{1}{2}$, $1\frac{1}{2}$; $^4F_{4\frac{1}{2}}$, $\Gamma=+4\frac{1}{2}$; $^4F_{3\frac{1}{2}}$, $\Gamma=0$; $^4F_{2\frac{1}{2}}$, $\Gamma=-3\frac{1}{2}A$; $^4F_{1\frac{1}{2}}$, $\Gamma=-6A$. A further consequence is that, in the case of all states consisting of a single level, that is, where either $s=0$ or $l=0$, Γ is equal to zero.

Of course all this is valid only when it is assumed that the multiplets show no more than small deviations from the Landé interval rule. In the case of a spectrum in which the levels are no longer arranged in multiplets at all, it may still be asserted however that Γ represents the separation of the levels from a hypothetical level, which would be realized if the interaction between the electron spin and the orbital motion were equal to zero.

Effects of Weak and Strong Magnetic Fields Upon the Γ Factors

According to the theory of the Zeeman effect, when the source of radiation is in a weak magnetic field, the vector representing the total impulse moment j of the atom has definite quantized orientations with respect to the direction of the field, while the angle between s and l remains unchanged. For a given value of j the values of Γ are consequently independent of the projection m of j upon the direction of the field and are the same as without a magnetic field.

In a strong magnetic field however, where the Paschen-Back effect occurs, the coupling between resultant s and resultant l is broken. Each has its own set of quantized orientations in the field, and each yields its own set of projections on the magnetic field, indicated respectively by m_s and m_l. In this case the angle between s and l is no longer constant

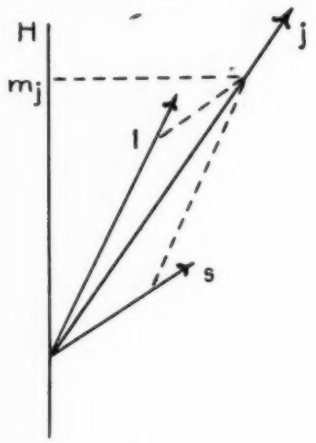

Fig. 1.

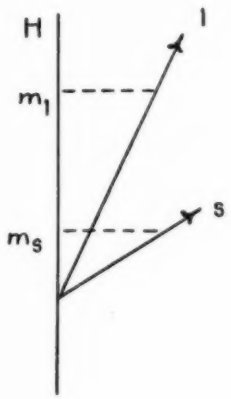

Fig. 2.

and the mean cosine of this angle has now a different value from that in the weak field. It may be found easily that the mean cosine between s and l is given in this case by

$$\overline{\cos(sl)} = \cos(sH)\cdot\cos(lH) = (m_s/s)(m_l/l)$$

In the case of a strong magnetic field the Γ values are therefore given by the formula:

$$\Gamma = Als\,\overline{\cos(ls)} = Am_s m_l. \tag{5}$$

Table IV gives the Γ values for a weak and a strong magnetic field for the simple case of a ^3D term, where $s=1$ and $l=2$. They are arranged in the table according to the values of the total projection m. In the case of a weak field m is simply the projection of j, while for the strong field it is given by $m=m_s+m_l$. The values for the weak field are therefore calculated by Eq. (4):

$\Gamma = Als\cos(ls) = \frac{1}{2}A\,[\,j(j+1)-l(l+1)-s(s+1)\,]$, where $l=2,\ s=1,\ j=3,\ 2,\ 1.$

We obtain the values of Γ for the strong field by Eq. (5):

$$\Gamma = Al\overline{\cos(ls)} = Am_s m_l, \text{ where } m_s = \pm 1, 0\ ;\ m_l = \pm 2, \pm 1, 0.$$

TABLE IV. Γ *values for* ^3D.

$m=$	-3	-2	-1	0	$+1$	$+2$	$+3$	
$j=3$	$+2A$	$+2A$	$+2A$	$+2A$	$+2A$	$+2A$	$+2A$	
$j=2$		$-A$	$-A$	$-A$	$-A$	$-A$		weak
$j=1$			$-3A$	$-3A$	$-3A$			field
$\Sigma\Gamma=$	$+2A$	$+A$	$-2A$	$-2A$	$-2A$	$+A$	$+2A$	
$m_s=-1$	$+2A$	$+A$	0	$-A$	$-2A$			
$m_s=0$		0	0	0	0	0		strong
$m_s=+1$			$-2A$	$-A$	0	$+A$	$+2A$	field

A given sum of Γ values, which is found from one vertical column, is the same for the weak as for the strong magnetic field. This is the result of the investigation of Landé.

Instead of introducing the energy of interaction between electron spin and orbital magnetic field, the magnetic energy in the external field divided by the field strength could have been substituted. It is well known that for a weak field this may be expressed by

$$m \cdot g \frac{h}{2\pi} \frac{e}{2mc}, \text{ where } g = 1 + \frac{j(j+1)+s(s+1)-l(l+1)}{2j(j+1)}$$

while for the strong field it is

$$(m_l + 2m_s) \cdot \frac{h}{2\pi} \cdot \frac{e}{2mc}.$$

Here again the sums of corresponding vertical columns are equal for the weak and strong fields, as Pauli has pointed out.

THE ASSEMBLING OF Γ VALUES

In order to calculate Γ values for cases of configurations of several electrons, it is necessary to make use of the same method which Pauli devised for the determination of g values, especially in the somewhat altered form introduced by the author[11] in which the quantum numbers, m_l and m_s were found to be useful.

Let it now be supposed that the atom is placed in a magnetic field so strong that the magnetic energy of each electron in the field is much stronger than the interaction energy of the electrons with one another. In that case to a first approximation each electron will orient itself in the field as if the other electrons were not present. The values of l_i and s_i for each electron

[11] S. Goudsmit, Zeits. f. Physik **32**, 794 (1925).

are now space quantized individually, so that each electron now has its own projections m_{l_i} and m_{s_i}, upon the direction of the field, subject however to the rule of Pauli that no two electrons may have all their quantum numbers exactly alike.

The Γ values of the entire atom are as before the sums of the γ_i values of the individual electrons. That is

$$\Gamma=\Sigma\gamma_i=\Sigma a_i m_{s_i} m_{l_i}. \tag{6}$$

A table of all possible values of Γ may now again be assembled for given values of the quantum numbers of the electrons, arranged according to the values of the total projection m. The values of m are found by adding together m_{l_i} and m_{s_i} for all the electrons in the configuration. That is

$$m=\Sigma(m_{l_i}+m_{s_i}). \tag{7}$$

There are thus as many m's as there are sets of quantum numbers m_{l_i} and m_{s_i} permitted by the Pauli restriction rule. These m values are not necessarily all different.

We now assert that the sum of all Γ *values belonging to a definite value of* m, *is independent of the strength of the field.* The corresponding result was announced by Pauli for the magnetic energies in an external field, divided by the strength of the field. We have succeeded with the help of these rules in determining the Γ values in certain isolated important cases.

The Γ Sum Rule Illustrated by the Case of Two Equivalent p Electrons

We will treat as an example the case of two equivalent p electrons. Then for both electrons, $l_1=l_2=1$, and $s_1=s_2=\frac{1}{2}$. Since we have chosen both electrons equivalent, the factor a_i is also the same for both. In the first

Table Va. *Two equivalent p-electrons.*

m_{s_1}	m_{l_1}	m_{s_2}	m_{l_2}	γ_1	γ_2	m_s	m_l	m	Γ
$+\frac{1}{2}$	+1	$+\frac{1}{2}$	0	$+\frac{1}{2}a$	0	+1	+1	+2	$+\frac{1}{2}a$
	+1		−1	$+\frac{1}{2}a$	$-\frac{1}{2}a$	+1	0	+1	0
	0		−1	0	$-\frac{1}{2}a$	+1	−1	0	$-\frac{1}{2}a$
$+\frac{1}{2}$	+1	$-\frac{1}{2}$	+1	$+\frac{1}{2}a$	$-\frac{1}{2}a$	0	+2	+2	0
	+1		0	$+\frac{1}{2}a$	0	0	+1	+1	$+\frac{1}{2}a$
	+1		−1	$+\frac{1}{2}a$	$+\frac{1}{2}a$	0	0	0	$+a$
	0		+1	0	$-\frac{1}{2}a$	0	+1	+1	$-\frac{1}{2}a$
	0		0	0	0	0	0	0	0
	0		−1	0	$+\frac{1}{2}a$	0	−1	−1	$+\frac{1}{2}a$
	−1		+1	$-\frac{1}{2}a$	$-\frac{1}{2}a$	0	0	0	$-a$
	−1		0	$-\frac{1}{2}a$	0	0	−1	−1	$-\frac{1}{2}a$
	−1		−1	$-\frac{1}{2}a$	$+\frac{1}{2}a$	0	−2	−2	0
$-\frac{1}{2}$	+1	$-\frac{1}{2}$	0	$-\frac{1}{2}a$	0	−1	+1	0	$-\frac{1}{2}a$
	+1		−1	$-\frac{1}{2}a$	$+\frac{1}{2}a$	−1	0	−1	0
	0		−1	0	$+\frac{1}{2}a$	−1	−1	−2	$+\frac{1}{2}a$

column of Table Va is given an assembly of all possible m_{l_i} and m_{s_i} values, which are so chosen according to the Pauli restriction rule that both electrons

never have the same complete set of quantum numbers. The second column gives the values of both γ_i's according to Eq. (5). The fourth gives the m values according to Eq. (7), and the last of the Γ values according to Eq. (6).

In Table IV we have already illustrated the operation of the Γ sum rule. We will now prepare two tables and make use of this rule to show how the sums of the Γ values may be calculated for the case under consideration. In Table Vb the values of Γ obtained in Va are arranged in vertical columns, according to the value of m with which each is associated, and the sums are calculated. We next consider the case of a weak field and recall that there will be a value of Γ for each value of j, but, since the interaction between l and s remains unaffected by the field, these values of Γ will be independent of m. (Compare Table IV) It is well known that a configuration of two p electrons yields two quantum states with $j=2$, one with $j=1$, and two with $j=0$. We indicate the corresponding Γ values by Γ_2', Γ_2'', Γ_1, Γ_0', and Γ_0'', respectively. These are assembled, in accordance with the considerations just given, in Table Vc. A comparison of Γ sums for like values of m yields us then

$$\Gamma_2'+\Gamma_2''=a/2\ ; \qquad \Gamma_1=-a/2\ ; \qquad \Gamma_0'+\Gamma_0''=-a.$$

TABLE Vb and c.

$m=$	-2	-1	0	$+1$	$+2$	
$m_s=+1$			$-\frac{1}{2}a$	0	$+\frac{1}{2}a$	b.
$m_s=0$	0	$+\frac{1}{2}a$	$+a$	$+\frac{1}{2}a$	0	strong
		$-\frac{1}{2}a$	0	$-\frac{1}{2}a$		field.
			$-a$			$m_l=m-m_s$
$m_s=-1$	$+\frac{1}{2}a$	0	$-\frac{1}{2}a$			
$\Sigma\Gamma=$	$+\frac{1}{2}a$	0	$-a$	0	$+\frac{1}{2}a$	
$j=2$	Γ_2'	Γ_2'	Γ_2'	Γ_2'	Γ_2'	
$j=2$	Γ_2''	Γ_2''	Γ_2''	Γ_2''	Γ_2''	c.
$j=1$		Γ_1	Γ_1	Γ_1		weak
$j=0$			Γ_0'			field
$j=0$			Γ_0''			
$\Sigma\Gamma=$	$\Gamma_2'+\Gamma_2''$	$\Gamma_2'+\Gamma_2''+\Gamma_1$	$\Gamma_2'+\Gamma_2''+\Gamma_1+\Gamma_0'+\Gamma_0''$	$\Gamma_2'+\Gamma_2''+\Gamma_1$	$\Gamma_2'+\Gamma_2''$	

This method therefore enables us to calculate the sums of the Γ *values for those levels which have equal j's*, just as Pauli has been able to treat the g sums. *These* Γ *sums will remain constant for all couplings.* The individual values of Γ can be determined however only in special cases, which we will discuss in what follows.

The most important application of the Γ sum rule is to be found in the Roentgen doublets. Here we have to do with a configuration of equivalent electrons, where just one is missing out of a complete group. In this case we find a double level, the doublet separation of which will in first approximation be due only to the interaction between the spin of each electron and

its orbit. If we consider a group of electrons, of which each has the same given value of l_i, the doublet levels will be found to have the j values: $j=l+\frac{1}{2}, j=l-\frac{1}{2}$. If we now make a table for this case similar to our Table V, we will find the vales of Γ to be: $\Gamma=-l_i a_i/2$ and $\Gamma=+(l_i-1)a_i/2$, for j equal to $l_i+\frac{1}{2}$ and $l_i-\frac{1}{2}$ respectively. In this case the values of Γ are completely determined. We find no Γ sums because there are no different levels with the same j. The Γ values found are therefore independent of the kind of coupling, and the doublet separations will under all circumstances be

$$\Delta\nu=\Delta\Gamma=-(l_i+\tfrac{1}{2})a_i=-\frac{R\alpha^2 Z_{\text{eff}}{}^4}{n^3 l_i(l_i+1)}$$

or the modified form of this expression given above for penetrating orbits. The coupling will in fact be very different in different cases. For inner orbits and high nuclear charge we expect the total resultant j to consist of the individual j_i of each of the electrons. For outer orbits and lower effective nuclear charge however we expect the ordinary Russell-Saunders coupling to be valid. We now know that the same doublet formula holds nevertheless for all cases. The reasoning given here is thus the proper proof of the validity of the Sommerfeld formula for Roentgen doublets.

By adding an s electron to a multiplet state one can prove in exactly the same way that in certain cases the total separation of the resulting multiplet with highest multiplicity is also independent of the coupling. This is illustrated, for example, by the fact that in the neon and argon spectra the separation of the s levels with $j=2$ and $j=0$ is exactly constant through the whole series of levels and equal to the p doublet of the ion.[12]

The Individual Γ Values

If we assume that the interaction between the spins of different electrons is much smaller than the interaction between the orbital magnetic field and the spin of each electron, then the individual Γ values for this case may be calculated in a simple manner. Moreover this special coupling affords a simpler method for the determination of Landé g sums, especially in cases of non-equivalent electrons.

With this coupling of the quantum vectors, each s_i and each l_i combine to form a resultant j_i. The γ_i value for each electron is calculated by Eq. (2a), and the sum of these values gives Γ for the whole atom. In our somewhat complicated example of two equivalent p electrons, j_i may have the value $1\frac{1}{2}$ or $\frac{1}{2}$. The corresponding γ_i values are $+\frac{1}{2}a_1$ and $-a_1$ respectively. If both electrons have $j_i=1\frac{1}{2}$, then $\Gamma=\gamma_1+\gamma_2=+a_1$. In this case the building rules of Pauli for two equivalent electrons give one state with the total impulse moment $j=0$, and one with $j=2$. If $j_i=1\frac{1}{2}$ for one electron and $j_i=\frac{1}{2}$ for the other, one state is obtained with $j=2$ and one with $j=1$, each with the Γ value, $\frac{1}{2}a_1-a_1=-\frac{1}{2}a_1$. If $j_i=\frac{1}{2}$ for each electron one state is obtained according to Pauli in which j is equal to zero, and for which Γ becomes $-2a_1$. These results may be tabulated as follows:

[12] S. Goudsmit and E. Back, Zeits. f. Physik **40**, 530 (1927).

$$
\begin{array}{llllll}
p^2: & j_1=1\tfrac{1}{2} & j_2=1\tfrac{1}{2} & j=0 & \Gamma=\tfrac{1}{2}a_1+\tfrac{1}{2}a_1=a_1 \\
 & & & j=2 & \quad=a_1 \\
 & j_1=1\tfrac{1}{2} & j_2=\tfrac{1}{2} & j=2 & \Gamma=\tfrac{1}{2}a_1- \quad a_1=-\tfrac{1}{2}a_1 \\
 & & & j=1 & \quad=-\tfrac{1}{2}a_1 \\
 & j_1=\tfrac{1}{2} & j_2=\tfrac{1}{2} & j=0 & \Gamma=-a_1-a_1=-2a_1 \\
 & & \text{For} & j=2 & \Sigma\Gamma=\tfrac{1}{2}a_1 \\
 & & \text{For} & j=1 & \Sigma\Gamma=-\tfrac{1}{2}a_1 \\
 & & \text{For} & j=0 & \Sigma\Gamma=-a_1.
\end{array}
$$

In most spectra there is a different coupling of the quantum vectors, the Russell-Saunders[13] coupling, which is responsible for normal multiplets. The spin moments of the individual electrons, s_i, form one resultant s, and the orbital moments, l_i, form a single resultant l. The total resultant j is then obtained by the combination of s and l.

In the case of only two electrons the mean cosines appearing in Eq. (3) may be calculated very simply, since they are constant. This calculation may be carried out as follows:

$$\frac{s_1}{s}\cos(s_1 s)=\frac{s_1(s_1+1)+s(s+1)-s_2(s_2+1)}{2s(s+1)}$$

$$\frac{l_1}{l}\cos(l_1 l)=\frac{l_1(l_1+1)+l(l+1)-l_2(l_2+1)}{2l(l+1)}$$

Our example of two equivalent p electrons yields us then the following results in the case of the Russell-Saunders coupling:

$$
\begin{array}{llllll}
^1S_0 & l=0 & s=0 & j=0 & \Gamma=0 \\
^1D_2 & =2 & =0 & =2 & =0 \\
^3P_2 & =1 & =1 & =2 & =+\tfrac{1}{2}a_1 \\
^3P_1 & =1 & =1 & =1 & =-\tfrac{1}{2}a_1 \\
^3P_0 & =1 & =1 & =1 & =-a_1.
\end{array}
$$

The total separation of ^3P is therefore $+\tfrac{1}{2}a_1-(-a_1)=1\tfrac{1}{2}a_1$.

Three Equivalent d Electrons

As soon as one has several equivalent electrons, more complicated methods must be employed, in order to be able to determine the separate Γ values for important cases of the Russell-Saunders coupling. We give here only one example, that of three equivalent d electrons.

If complete tables are made for this example corresponding to Tables Va, Vb, and Vc, for the other example, the following results are obtained:

[13] H. N. Russell and F A Saunders, Astrophys. J. **61**, 38 (1925).

1	Level for which	$j=5\frac{1}{2}$,	$\Gamma=$	$\frac{1}{2}a_1$
3	Levels "	" $j=4\frac{1}{2}$,	$\Sigma\Gamma=$	$1\frac{1}{2}a_1$
3	" "	" $j=3\frac{1}{2}$,	$\Sigma\Gamma=$	$-a_1$
4	" "	" $j=2\frac{1}{2}$,	$\Sigma\Gamma=$	0
4	" "	" $j=1\frac{1}{2}$,	$\Sigma\Gamma=$	$-2\frac{1}{2}a_1$
3	" "	" $j=\frac{1}{2}$,	$\Sigma\Gamma=$	$-1\frac{1}{2}a_1$.

The value of Γ is thus uniquely determined only in the case of the first level, for which $j=5\frac{1}{2}$. We obtain only the sums for the other values of j.

Let us now make the special assumption however, that we have here the Russell-Saunders coupling and consequently normal multiplets. This configuration will then give the following multiplets:

$$^4F',\ ^4P',\ ^2H',\ ^2G,\ ^2F',\ ^2D,\ ^2D,\ ^2P'.$$

If we take as unknowns the single values of A corresponding to each of these normal multiplets, we can express the Γ's in terms of these A values by means of Eq. (4). We thus have eight unknowns and the determined Γ sums give us only six equations for them. Moreover these equations will be found to be not independent. For example we cannot separate the unknown A values for the two expected ^2D states. We must therefore first apply another method.

This is to make use of the fact that, if each multiplet is considered separately, the sums of the Γ values will be the same in weak and strong magnetic fields, as is also the case with the g values. We would be prepared to apply this method if we could only tell which configurations from the table, constructed for this example after the manner of Table V, would give a certain one of these multiplets. This is not possible for all configurations, but for just a sufficient number to determine the values of A for our multiplets.

If we consider for instance the ^4F level in a strong magnetic field, among the levels which arise there is one with the projections $m_l=3$ and $m_s=3/2$, giving $m=4\frac{1}{2}$. This level originates from the $^4F_{4\frac{1}{2}}$ level, that being the only one which can have $m=4\frac{1}{2}$. Now indeed our table, alluded to above, gives one configuration for which

$$m_s=\Sigma m_{s_i}=1\tfrac{1}{2},\ \text{and}\ m_l=\Sigma m_{l_i}=3,$$

viz. $$m_{s_1}=m_{s_2}=m_{s_3}=+\tfrac{1}{2}\ ;\ \text{and}\ m_{l_1}=2,\ m_{l_2}=1,\ m_{l_3}=0.$$

For this configuration we find: $\Gamma=\Sigma a_1 m_{l_i} m_{s_i}=1\frac{1}{2}a_1$. As this is the only one of the ^4F levels with $m=4\frac{1}{2}$, this Γ will be the same in a weak field and it follows thus that $\Gamma=1\frac{1}{2}a_1$ for $^4F_{4\frac{1}{2}}$. If we denote the A value of this multiplet by $A(^4F)$, we find from Eq. (4) and the example on page 5, $A(^4F)=a_1/3$, and for the total separation

$$\Delta\nu=10\tfrac{1}{2}A(^4F)=7a_1/2$$

We use the same process once more to determine Γ for the $^4P_{2\frac{1}{2}}$ level. After that we can finally use the six equations given by the determined Γ sums and find the results as given in Table I. This example is the most complicated one. In the other cases the results can be obtained much more simply but by using the same methods.

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MULTIPLET SEPARATIONS

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Abstract

Formulas for the separations of normal multiplets, arising from general configurations, are derived by reasoning from the fundamental assumption that they are due to the interaction energy between spin and orbital magnetism of the electrons. The separations are known for multiplets arising from groups of equivalent electrons, from considerations given in the preceding paper. It is shown in this investigation, by a simple treatment of the vector model, that the interaction energy for other configurations may be found in terms of that of the equivalent group and the interaction energy of the electron or group of electrons added, provided the quantum vectors of the original configuration remain unchanged. Our treatment applies only to multiplets showing reasonably close agreement with the interval rule, and which are therefore accounted for by the Russell-Saunders coupling. Examples given for illustration are taken from data on Fe and O^+. Calculated results indicate the validity of our formulas to the extent permitted by agreement of data with the interval rule.

MULTIPLET separations are due to the energy of interaction between spin and orbital magnetism of the electrons. The value of this energy for a single electron is indicated by γ and is given by the formula:

$$\gamma = als \cos (ls) \tag{1}$$

In this formula, $a = R\alpha^2 Z^4/[n^3 l(l+1/2)(l+1)]$ for a Kepler orbit, in first approximation, or $a = R\alpha^2 Z_i^2 Z_a^2/[n^3 l(l+1/2)(l+1)]$ for a penetrating orbit. Also $s = 1/2$ and $l = 0$, 1, 2 etc., depending on the type of orbit. When only one electron is responsible for the spectrum and we thus have a doublet, the two possible values of γ give the separations of the actual levels from the position of the hypothetical level without interaction energy.

When we have multiplets due to configurations of two or more electrons, it is sufficient in most cases to consider only the interaction between the spin of each electron and its own orbit. While there is some energy due to interaction between the spin of a given electron and the orbit of another, it is proportional to a lower power of the nuclear charge, and, for purposes of this discussion, need not be considered.[1]

Suppose we have an atom in which the so-called Russell-Saunders coupling occurs. All the electronic spins s_i form a resultant s, and all orbital moments form a resultant l, while s and l combine finally to give a total resultant j. The total interaction energy between the spins and respective orbits of the electrons is then:

$$\Gamma = \sum a_i l_i s_i \overline{\cos (l_i s_i)}$$

In this ideal case it may be easily shown that

$$\overline{\cos (l_i s_i)} = \overline{\cos (l_i l)} \cos (ls) \overline{\cos (s_i s)}$$

[1] For the interesting case of the helium triplet in which these terms must be considered, see W. Heisenberg, Zeits. f. Physik 39, 499 (1926).

Thus the interaction energy is of the form:

$$\Gamma = Als\cos(ls), \text{ in which } A = \sum_i (l_i/l)\cos(l_i l)(s_i/s)\cos(s_i s) \qquad (2)$$

The different levels of the same multiplet all have the same coefficient A. Γ is however determined by $\cos(ls)$ according to the formula:[2]

$$\Gamma = Als\cos(ls) = \tfrac{1}{2}A[j(j+1)-l(l+1)-s(s+1)]$$

This formula will be recognized as the familiar interval rule of Landé. If we take the energy difference between two levels of the same multiplet, one having a total moment j and the other $j-1$, we find:

$$\Gamma(j)-\Gamma(j-1)=Aj.$$

The subsequent intervals are thus proportional to the larger value of j corresponding to one of the two adjacent levels. We find the factor A for each multiplet by dividing the multiplet separations by these interval factors equal to j. If we take for instance a ^4D level, $s=3/2$, $l=2$, and j can have the values $7/2$, to $1/2$, as resultant of s and l. The three intervals between these four levels are proportional to $7/2$, $5/2$ and $3/2$, the proportionality factor being just A.

In a previous paper one of us[3] derived formulas for the values of Γ or A in cases where we have only a number of equivalent electrons. It was possible to express A in terms of the values of a_i for the single electrons, which of course are all equal if we take only equivalent electrons.

In this investigation we will show that it is possible to determine A for other configurations of electrons. In general the method will be to consider the addition of another electron to a group for which A is known, and to obtain a new A in terms of that of the original group and a_i of the new electron. Or the expression for A may be in terms of the values of a_i for the different electrons. Likewise the total multiplet separations may be determined in terms of the different values of a_i. The latter method is somewhat more convenient for application, as it gives at the same time an average value in cases where the interval rule does not hold strictly.

Before proceeding to a derivation of the expression for A it is necessary to state the conditions under which we may consider the result of adding a new electron to a given configuration. A solution of Eq. (2) must involve an evaluation of $\cos(l_i l)$ and of $\cos(s_i s)$. This makes it necessary that the quantum vectors be determined in a definite fashion. Accordingly we must impose the following restriction, which the accompanying figure will help make clear. The values of l_i and s_i of the original group combine separately, according to the Russell-Saunders scheme, to yield resultant quantum vectors which we designate by l' and s'. These vectors are not to be disturbed or

[2] This expression for the cosine of the angle between two quantum vectors was originally found as an empirical relationship by Landé, but has now been verified by the application of new mechanics.

[3] Goudsmit, Phys. Rev. **31**, 946 (1928). Preceding paper in this issue.

altered by the addition of a new electron. We then obtain the resultant vectors, l and s, of the new configuration, by combining l' with l_2 of the added electron, and s' with s_2. In making this composition we consider l' and s' as single vectors and are entirely unconcerned as to their origin. The total resultant, that is of l and s, we again call j.

This special case will not occur very often, since the resultant, l' and s', of the electrons already present will usually be disturbed by the addition of the new one, and one cannot say that the new resultant l is built up of the old l' and the added l_2 and similarly for s, which is essential for the discussion to follow. It will appear however that our formula for A is applicable in cases where the interval rule holds fairly well. Two cases may be mentioned

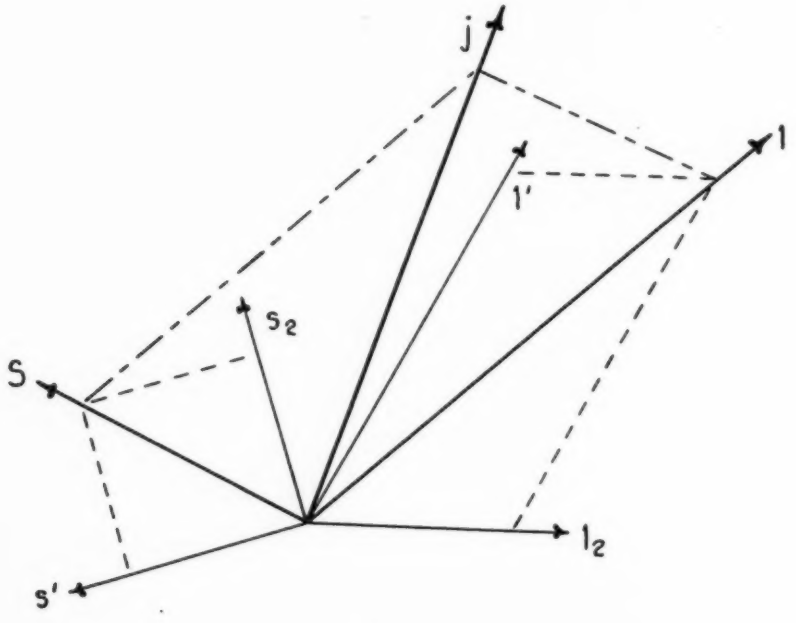

Fig. 1.

as examples in which we are quite certain that the restriction, as to the relation of the quantum vectors of the new electron with the resultant vectors of the original group, is valid.

If we have a group of equivalent electrons and add another kind of electron, the resultant quantum vectors will be formed as indicated above, since the interaction between the equivalent electrons will in general be stronger than between them and the new one.

A simpler case is to be found in the addition of a second electron to an atom having only one valence electron. Here it is certain that the new electron cannot change the quantum vectors, l_1 and s_1, of the original one. Consequently resultant l is obtained by the combination of l_1 and l_2, and resultant s from s_1 and s_2.

It must be remembered however that these results are not perfectly general. In all cases we assume that we are to get normal multiplets, to which the interval rule may be applied with reasonable success. These occur when the vectors have the so-called Russell-Saunders coupling, in which the spins always form a resultant spin moment s, while the orbital moments combine to form a resultant l.

It is now possible to express the total interaction energy in terms of the coefficients A' and a_2 of the original multiplet and the added electron. If we apply Eq. (2) to this case we get:

$$A = A'(l'/l)\cos(l'l)\,(s'/s)\cos(s's) + a_2(l_2/l)\cos(l_2l)\,(s_2/s)\cos(s_2s).$$

Since s is the resultant of only two vectors, s' and s_2, we can write for the cosines involved:

$$\frac{s'}{s}\cos(s's) = \frac{s(s+1)+s'(s'+1)-s_2(s_2+1)}{2s(s+1)}$$

and

$$\frac{s_2}{s}\cos(s_2s) = \frac{s(s+1)+s_2(s_2+1)-s'(s'+1)}{2s(s+1)}.$$

In the same way

$$\frac{l'}{l}\cos(l'l) = \frac{l(l+1)+l'(l'+1)-l_2(l_2+1)}{2l(l+1)}$$

and

$$\frac{l_2}{l}\cos(l_2l) = \frac{l(l+1)+l_2(l_2+1)-l'(l'+1)}{2l(l+1)}.$$

We thus obtain the result:

$$\begin{aligned} A = A'&\frac{s(s+1)+s'(s'+1)-s_2(s_2+1)}{2s(s+1)} \times \frac{l(l+1)+l'(l'+1)-l_2(l_2+1)}{2l(l+1)} \\ &+ a_2\frac{s(s+1)+s_2(s_2+1)-s'(s'+1)}{2s(s+1)} \times \frac{l(l+1)+l_2(l_2+1)-l'(l'+1)}{2l(l+1)}. \end{aligned} \tag{3}$$

This formula, applied to the triplet arising from two valence electrons, is identical with that given by Heisenberg,[4] who obtained the following equation, expressed in our notation, long before the meaning of the different quantum vectors was quite clear.

$$A = A'\frac{1}{2}\,\frac{l(l+1)+l_1(l_1+1)-l_2(l_2+1)}{2l(l+1)} + a_2\frac{1}{2}\,\frac{l(l+1)+l_2(l_2+1)-l_1(l_1+1)}{2l(l+1)}.$$

That this follows, in the case of two electrons, from Eq. (3) is clear when we remember that $s_1 = s_2 = 1/2$.

[4] W. Heisenberg, Zeits. f. Physik **32**, 841 (1925).

In order to illustrate the application of our formulas we have chosen examples from published data on the iron spectrum with sufficient material on ionized iron to show the building up of the configurations. An example is

TABLE I.

Electron configuration	Equation (3)	Separation factor from adjacent levels / total separation	A'' $d^{6}{}^{5}D$
Fe III d^6	^5D $A=A''$		exp. >120
Fe II d^6s			
$l''=2$, $s''=2$, ^5D+s	^6D $A'=4A''/5$	$A'=$ 86, 81, 78, 76 82	102
$l_3=0$, $s_3=1/2$	^4D $A'=6A''/5$	=125, 115, 111 119	99
Fe I d^6s^2	^5D $A=A''$	$A=$104, 96, 92, 90 98	98
d^6s, s			
$l'=2$, $s'=5/2$, ^6D+s	^7D $A=2A''/3$	$A=$ 69, 68, 66, 65 68	102
$l_3=0$, $s_3=1/2$, $A'=4A''/5$	^5D $A=14A''/15$	= 93, 91, 88, 86 92	99
$l'=2$, $s'=3/2$, ^4D+s	^5D $A=9A''/10$	=105, 93, 82, 43 (91)	(101)
$l_3=0$, $s_3=1/2$, $A'=6A''/5$	^3D $A=3A''/2$	=106, 160 (128)	(86)
other coupling:		This coupling does not give right results for A''	
$l''=2$, $s''=2$, $^5D+^1S$	^5D $A=A''$		
$l_3=0$, $s_3=0$ or 1, $^5D+^3S$	^5D $A=5A''/6$	$\Sigma A=11A''/6$ for quintets 183	99
		independent of coupling	
d^6s, p		calc.	
$l'=2$, $s'=5/2$, $^6D=p$	^7F $A=4A''/9-a_3/18$	$A=$ 32, 30, 28, 27, 26 26 28 30	
$l_3=1$ $s_3=1/2$, $A'=4A''/5$	$^7D'$ $=5A''/9-a_3/36$	= 42, 49, 49, 54 50 48	
	^7P $=A''+a_3/12$	=117, 119 135 118	
	^5F $A=28A''/45+a_3/18$	= 58, 57, 55, 53 57	
	$^5D'$ $=7A''/9+a_3/36$	= 60, 67, 70, 71 65	
	^5P $=7A''/5-a_3/12$	=138, 132 135	
$l'=2$, $s'=3/2$, ^4D+p	^5F $A=3A''/5-a_3/12$	$A=$ 69, 72, 73, 73 70	
$l_3=1$, $s_3=1/2$, $A'=6A''/5$	$^5D'$ $=9A''/10-a_3/24$	=103, 98, 108, 105 103	
	^5P $=27A''/20+a_3/8$	=130, 126 129	
	^3F $A=5A''/6+a_3/12$	$A=$125, 110 119 118	
	$^3D'$ $=25A''/24+a_3/24$	=121, 126 125 123	
	^3P $=15A''/8-a_3/8$	=208, 193 243 203	
Other possible coupling $d^5(sp)$: $^5D+^3P$, $^5D+^1P$		This coupling gives no good agreement. The following sums are independent of the coupling:	
		sextets $\Sigma A=2A''$ 192	96
		quintets $\Sigma A=113A''/120$ 558	98
		triplets $\Sigma A=15A''/4$ 444	118
		F terms $\Sigma A=5A''/2$ 274	110
		D' terms $\Sigma A=131A''/40$ 339	103
		P terms $\Sigma A=45A''/8$ 580	103
		Total $\Sigma A=57A''/5$ 1194	105
		calc. $a_3/72\sim 5$	
Fe II d^7	$^4F'$ $A=A'$	$A=$123, 116, 112 $A'd'=$118	118
	$^4P'$ $A=A'$	= 80, 154 (108)	(108)
Fe I d^7s			A'
$l'=3$, $s'=3/2$, ^5F+s	$^5F'$ $A=3A'/4$	$A=$ 90, 88, 86, 85 4s 88	117
$l_3=0$, $s_3=1/2$		= 74, 94, 94, 92 5s (87)	(117)
	$^3F'$ $A=5A'/4$	=146, 136 4s 142	114
		=144, 134 5s 140	112
$l'=1$, $s'=3/2$, ^4P+s	$^5P'$ $A=3A'/4$	$A=$ 58, 100 (75)	
$l_3=0$, $s_3=1/2$,	$^3P'$ $A=5A'/4$	= 54, 105 (71)	
d^7p			
$l'=3$, $s'=3/2$, ^4F+p	$^5G'$ $A=9A'/16+a_3/16$	$A=-10$, 95, 88, 82 (56)	
$l_3=1$, $s_3=1/2$	^5F $A=11A'/16+a_3/48$	= 67, 62, 59, 56 63	
	$^5D'$ $A=A'-a_3/12$	= 89, 87, 87, 87 87	
	$^3G'$ $A=15A'/16-a_3/16$	$A=$ 78, 78 78	
	^3F $A=55A'/48-a_3/48$	=119, 120 119	
	$^3D'$ $A=5A'/3+a_3/12$	=168, 159 164	
		G' terms $\Sigma A=3A'/2$ (134)	(89)
		F terms $\Sigma A=11A'/6$ 182	99
		D' terms $\Sigma A=8A'/3$ 251	98
		quintets $\Sigma A=9A'/4$ (206)	(92)
		triplets $\Sigma A=15A'/4$ 363	97
		total $\Sigma A=6A'$ (569)	(95)

also taken from the spectrum of ionized oxygen. The iron spectrum is very satisfactory for this purpose because a very complete and evidently correct analysis of it has been made, and also because it exhibits a large number of multiplets which obey the interval rule closely enough to satisfy our theory.

A very brief explanation of the tables will suffice. In the example from the iron spectrum, we begin with Fe^{++} having the configuration d^6 which yields a ^5D term. All interesting configurations of Fe^+, from which Fe is derived, are built upon this d^6 group.[5]

The values of the separation factor, determined from adjacent levels and the total separation and indicated in Column 3, are introduced to show how closely the interval rule is obeyed in a given multiplet. Equal numbers for a given multiplet would indicate perfect conformity with the interval rule. All bracketed values of the separation factor are derived from examples showing very poor agreement with the interval rule.

In all cases the value of the separation factor for the equivalent d^6 or d^7 group, for which the given configuration is derived, is calculated. The values obtained are tabulated in the last column. These should be equal except for the screening effect of the outer electrons added. In the d^6 case the values of A'' are very nearly constant, indicating that the added electrons do not change the screening due to six d electrons by a very large amount. The

TABLE II

Electron configuration	Equation (3)	Separation factor from adjacent levels	total separation	A'
O II s^2p^2s				$A'(p^2)$
$l'=1$, $s'=1$, ^3P+s	$^4P'$ $A=2A'/3$	$A=$ 64, 70	$3s$ 66	99
$l_2=0$, $s_2=1/2$		= 65, 70	$4s$ 67	100
	$^2P'$ $A=4A'/3$	=120	$3s$ 120	90
		=125	$4s$ 125	94
^1D+s	^2D $A=0$	$=-0.4$	$3s$ -0.4	
		$=-0.3$	$4s$ -0.3	
p^4s				$A'(p^4)$
^5P+s	$^4P'$ $A=2A'/3$	$A=-65, -55$	-61	-91
	$^2P'$ $A=4A'/3$	$=-115$	-115	-86
^3D+s	^2D $A=0$	$=-4$	-4	
s^2p^2p				
^5P+p	^4P $A=A'/3+a_3/6$	$A=$ 37, 31	34	
	$^4D'$ $=A'/3+a_3/6$	= 36, 37, 37	36	
	^2P $=2A'/3-a_3/6$	= 40	40	
	$^2D'$ $=2A'/3-a_3/6$	= 76	76	
		Total $\Sigma A=2A'$	186	93
^3D+p	^3P $A=0-a_3/2$	$A=$ 31	31	
	$^3D'$ $=0+a_3/6$	$=-8$	-8	
	^3F $=0+a_3/3$	= 7	7	

deviations from the mean value in the A'' column are in general smaller than the deviations from the interval rule in many multiplets, and may doubtless be ascribed to this poor agreement with the interval rule, which would actually lead us to expect larger variations of A'' than are found.

In the case of configurations built upon the d^7 group, we find that an added s electron does not change the screening very much, but that it is changed considerably by the addition of a p electron. If we consider d^7s or d^7p; configurations separately we have excellent agreement in the A' values obtained from different multiplets.

[5] An almost complete term table in accordance with the classification of Laporte is given by W. F. Meggers, Astrophys. J. **60**, 60 (1924). For a discussion of the assignment of levels, see O. Laporte, Proc. Nat. Acad. Sc. **12**, 496 (1926). The lowest levels of Fe^+ are given by H. N. Russell, Astrophys. J. **64**, 194 (1926).

In the O^+ example[6] we have the interesting case discussed in the previous paper. Since six p electrons constitute a complete shell, we should obtain the same value of A' derived from p^2s as from p^4s, except that the algebraic sign would be negative in the latter case and the value should be slightly smaller because of the somewhat larger screening of four p electrons. This is actually observed, and we also find good agreement in the A' values of different multiplets if we consider p^2s and p^4s separately.

When we consider p^2p configurations of O^+ we find that both quartets, ^4P and $^4D'$, show good agreement in the values of the separation factor, but that the doublets show considerable deviation. This may be due to lack of agreement with the interval rule but this cannot be concluded definitely, because it is not possible to say whether the interval rule is obeyed or not in the case of doublets.

We expect this method to be useful in checking the assignment of configurations and terms in complicated cases. Calculations, not included in this paper, on the quintets of Ti I, and the quartets of Ti II, came out in agreement with the assignment made by Russell.[7] Also the separations in the O III[8] spectrum are in perfect agreement with the formulas given here.

DEPARTMENT OF PHYSICS,
UNIVERSITY OF MICHIGAN,
February, 1928.

[6] For a complete term table, see H. N. Russell, Phys. Rev. **31**, 27 (1928).
[7] H. N. Russell, Astrophys. J. **66**, 283 (1927) also **66**, 347 (1927).
[8] A. Fowler, Proc. Royal Soc. January, 1928.

SERIES SPECTRUM OF SODIUM, Na_{II}

By I. S. Bowen

Abstract

Seventy-four lines in the sodium spark spectrum are classified as combinations between twenty-three terms of Na_{II}. The ionization potential of Na_{II} is fixed at 47.0 ± 0.5 volts.

THE spark spectrum of sodium has been obtained by Schillinger,[1] by Foote, Meggers and Mohler,[2] and more recently by Newman,[3] who also found a large number of constant frequency differences. It has now been

TABLE I. *Series lines in Na_{II}.*

Int.	λ (I. A.)	ν	Series Designation	Int.	λ (I. A.)	ν	Series Designation
2	372.04	268788.	$2p-3s_2$	4	3015.80	33149.1	$3p_8-X_7$
1	376.34	265717.	$2p-3s_4$	4	3029.56	32999.5	$3p_3-X_1$, $3p_3-X_8$
1	2506.27	39888.1	$3p_{10}-X_1$	4	3037.32	32914.2	$3p_8-X_9$
1	2515.57	39740.5	$3p_{10}-X_2$	3	3045.97	32820.8	$3p_4-X_3$
4	2531.64	39488.2	$3p_{10}-X_3$	5	3056.30	32709.9	$3s_8-3p_8$, $3s_-3p_8$
7	2612.10	38271.9	$3p_{10}-X_8$	1	3064.86	32618.4	$3p_7-X_7$
6	2661.65	37559.5	$3p_{10}-X_7$	1	3066.73	32598.6	$3p_2-X_1$
6	2671.90	37415.5	$3p_{10}-X_6$	5	3078.55	32473.4	$3s_4-3p_7$, $3p_7-X_8$
5	2678.25	37326.8	$3p_{10}-X_9$	1	3080.30	32455.0	$3p_2-X_2$
6	2809.73	35580.2	$3s_8-3p_2$	8	3092.98	32321.8	$3s_8-3p_9$
1	2818.58	35468.4	$3p_8-X_1$	3	3104.52	32201.8	$3p_2-X_3$
1	2830.01	35325.2	$3p_8-X_2$	0	3107.69	32168.9	$3p_2-X_4$
7	2841.99	35176.3	$3s_8-3p_3$	3	3124.64	31994.5	$3p_8-X_6$
3	2859.64	34959.2	$3s_8-3p_4$	7	3129.55	31944.3	$3s_4-3p_8$
0	2861.34	34938.4	$3p_7-X_1$	4	3135.69	31881.8	$3s_3-3p_7$
3	2871.53	34814.5	$3s_-3p_2$	0	3146.05	31766.7	$3p_2-X_4$
0	2873.13	34795.1	$3p_7-X_2$	4	3149.51	31741.3	$3s_2-3p_2$
5	2881.38	34695.5	$3p_8-X_1$?	5	3164.16	31594.9	$3p_8-X_7$
3	2886.42	34634.9	$3p_8-X_4$	2	3179.29	31444.5	$3p_8-X_8$
4	2894.19	34541.9	$3p_7-X_3$	5	3190.05	31338.4	$3s_2-3p_3$
6	2905.11	34412.0	$3s_4-3p_3$	5	3212.44	31120.1	$3s_2-3p_4$
6	2917.78	34262.6	$3s_8-3p_8$	0	3216.60	31079.8	$3p_3-X_8$
5	2919.34	34244.3	$3p_9-X_8$	2	3226.16	30987.7	$3p_2-X_8$
4	2921.14	34222.9	$3s_3-3p_2$	3	3235.07	30902.4	$3p_4-X_7$
2	2923.67	34193.6	$3s_4-3p_4$	1	3251.22	30748.9	$3p_4-X_8$
0	2931.62	34101.0	$3p_7-X_4$	5	3258.38	30681.4	$3p_2-X_6$, $3p_2-X_7$
1	2945.92	33935.2	$3p_9-X_6$	0	3260.45	30661.8	$3p_4-X_9$
3	2947.56	33916.5	$3p_6-X_1$	3	3274.36	30531.6	$3p_3-X_8$
7	2951.50	33871.2	$3p_8-X_4$	7	3285.86	30424.7	$3s_2-3p_6$
1	2952.83	33855.9	$3p_8-X_5$	3	3318.14	30128.7	$3p_2-X_8$
1	2960.11	33772.7	$3p_6-X_2$	3	3327.81	30041.3	$3p_2-X_9$
5	2975.24	33600.9	$3s_3-3p_4$	0	3373.26	29636.4	$3s_2-3p_8$
5	2979.96	33547.7	$3p_8-X_6$	–	3400.2	29401.4	$3s_2-3p_7$
0	2981.03	33535.7	$3p_9-X_7$	1	3462.68	28871.1	$3s_2-3p_8$
5	2984.45	33497.2	$3s_4-3p_6$	10	3533.03	28296.2	$3s_8-3p_{10}$
2	3007.65	33238.9	$3s_8-3p_7$	8	3631.37	27530.0	$3s_4-3p_{10}$
2	3009.60	33217.4	$3p_4-X_1$	3	3711.2	26938.	$3s_2-3p_{10}$

[1] Shillinger, Akad. Wiss. Wien Sitz-Ber. **118**, 11 (1909).

[2] Foote, Meggers and Mohler, Astrophys. J. **55**, 145 (1922).

[3] Newman, Phil. Mag. **5**, 150 (1928).

possible to classify all but ten of the lines of intensity greater than 1. The lines thus identified are given in Table I. The wave-lengths above 2000A are taken from Newman.

The relative intensities and separations of the lines of the $3s-3p$ group follow closely those found in the spectra of other eight-electron systems, such as Ne_I, A_I, K_{II}, Ca_{III}. This leaves little doubt as to the identification of the lines in this group, with the possible exception of those involving the p_5 level.

The remaining levels originate from the configurations for which the excited electron is in either a $3d$ or a $4s$ orbit. Since these configurations are predicted to have almost identical energies it is in most cases quite impossible to differentiate between the terms arising from them. Consequently all of these levels are designated with an X. It is quite probable that X_1 is the $4s_2$ level and X_3 the $4s_3$ level. $4s_5$ should have a term value about 2000 cm^{-1} greater than these and therefore falls near the position of X_7 which has the proper inner quantum number. Assuming this identification and making this X_7 term and the $3s_5$ term fit a Ritz formula similar to that which

TABLE II. *Term values in Na_{II}.*

Term	J	Value	Term	J	Value
$3s_2$	1	112161.5	$3p_8$	2	83290.3
$3s_3$	0	114642.5	$3p_9$	3	83678.2
$3s_4$	1	115234.5	$3p_{10}$	1	87704.3
$3s_5$	2	116000.0			
			X_1	1	47821.0
$2p$	0	380950.	X_2	1–2	47964.8
			X_3	0	48218.4
$3p_2$	1	80419.9	X_4	1	48655.3
$3p_3$	2	80823.1	X_5	2	49433.2
$3p_4$	1	81041.2	X_6	2	49742.9
$3p_5$	0	82525.1	X_7	2	50142.0
$3p_6$	2	81737.2	X_8	1–2	50291.3
$3p_7$	1	82760.7	X_9	1–2	50377.9

describes the corresponding series in neon the term values given in Table II are obtained. Regardless of the validity of the identification of these $4s$ terms the values can hardly be in error by more than a very few thousand frequency units since the d levels should be nearly hydrogen-like and therefore must have term values in the neighborhood of 48770 cm^{-1}. All of the X terms, part of which are certainly $3d$ terms, fall within 2000 cm^{-1} of this value. These terms fix the ionization potential at 47.0 ± 0.5 volts.

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THE SPECTRUM OF GOLD CHLORIDE

By W. F. C. Ferguson

Abstract

The spectrum of gold chloride vapor excited by streaming active nitrogen was photographed. It was found to consist of 43 bands comprising, for each isotope of AuCl, two intermingled systems in the green region. All the bands are shaded toward the red. No other bands were found between λλ7000–2000. The band heads of each system were measured, and equations are given representing their positions. Agreement with theory was found for the isotopic displacement of the band heads due to the chlorine isotopes. The vibrational intensity distribution agrees with that theoretically expected from the observed relative values of the initial and final vibrational frequencies. Attempts to excite spectra of gold bromide and iodide in a similar manner were without success.

General Procedure

VAPOR from gold trichloride ($AuCl_3$) was introduced into a stream of active nitrogen after the method originated by Strutt and Fowler,[1] as recently used by Mulliken.[2] The spectrum thus excited was examined in the region λλ7000–2000 and, except for certain atomic lines, was found to consist only of a number of bands in the green. These bands are all shaded toward the red. A reproduction of the bands is given in Fig. 1.

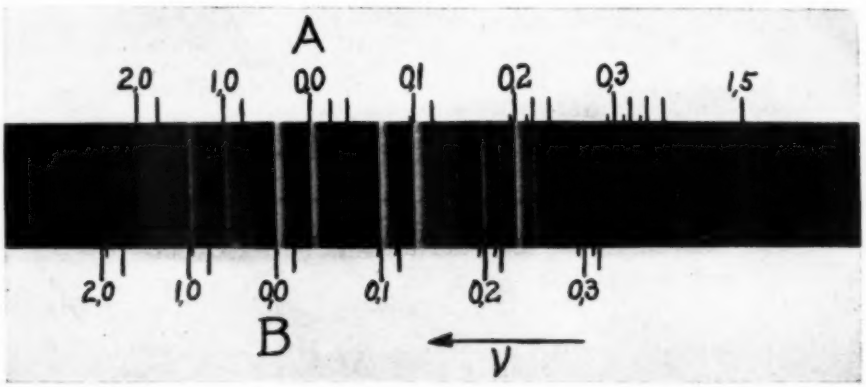

Fig. 1. Spectrum of gold chloride excited by active nitrogen. Bands of the *A* system are marked by vertical lines above; bands of the *B* system are marked below. Each $AuCl^{35}$ head is indicated by a long line; each $AuCl^{37}$ head by a short line.

The photograph used for measurement was made with a quartz spectrograph giving a dispersion in the green of about 28A per mm. An Eastman astronomical green sensitive plate was used, with an exposure of about three hours. The measurements of the band heads are given in Tables I and II.

[1] R. J. Strutt and A. Fowler, Proc. Roy. Soc. **A86**, 105 (1911).
[2] R. S. Mulliken, Phys. Rev. **26**, 1 (1925).

TABLE I. *A Bands.* Column n' n'' gives the vibrational quantum numbers; O–C, observed minus calculated values of wave number, calculated values being obtained from the formulas given in this paper.

		$AuCl^{35}$ heads				$AuCl^{37}$ heads			
n'	n''	Int.	λ (I. A.)	Wave-no.	O−C	Int.	λ (I. A.)	Wave-no.	O−C
2	0	1	5075.0	19699.	1				
3	1	00	94.1	625.	−1				
1	0	4	5155.90	389.9	1				
2	1	000	75.6	316.	−2				
0	0	5	5240.02	078.6	0				
1	1	0	60.6	004.	−5				
2	2	0	78.4	18940.	−1				
0	1	5	5346.65	698.1	0	0	5344.4	18706.	−2
1	2	0	65.6	632.	1				
0	2	4	5456.76	320.8	0	1	5451.1	340.	1
1	3	2	76.01	256.4	0	0	70.1	276.	0
2	4	0	95.4	192.	−1				
0	3	2	5570.4	17947.	1	0	5562.1	17974.	1
1	4	2	90.20	883.5	0	0	81.6	911.	−1
2	5	1	5609.5	822.	−1	00	5601.6	847.	−6
3	6	00	30.0	757.	−7				
1	5	00	5706.8	518.	4				

TABLE II. *B bands.*

		$AuCl^{35}$ heads				$AuCl^{37}$ heads			
n'	n''	Int.	λ (I. A.)	Wave-no.	O−C	Int.	λ (I. A.)	Wave-no.	O−C
2	0	1	5041.74	19828.9	0	1	5046.6	19810.	−5
3	1	0	61.4	752.	−4				
1	0	4	5121.95	518.4	0	00	5123.4	513.	1
2	1	0	40.8	447.	−2				
0	0	5	5205.53	205.0	0				
1	1	000	23.2	140.	2				
0	1	5	5310.61	18825.0	0	1	5308.24	18833.4	−1
1	2	1	29.0	760.	−1	000	26.7	768.	−4
0	2	3	5419.43	447.	0	1	5414.2	465.	0
1	3	2	37.56	385.5	0	0	31.8	405.	0
0	3	1	5531.67	072.8	1	00	5523.0	101.	2
1	4	1	49.89	013.4	0	0	41.1	042.	1

In addition to the bands, the gold lines at λλ4792.6, 3122.8, 3029.2, 2748.3, 2776.0, 2641.5, 2428.0, and 2352.7 appeared on the plates.

ANALYSIS OF BANDS

From its structure, the observed band spectrum is obviously that of a diatomic molecule, presumably AuCl. Most of the strong heads are accompanied each by a closely adjacent weak head (cf. Fig. 1) the two heads being

interpreted as due to $AuCl^{35}$ (stronger) and $AuCl^{37}$ (weaker). It was found possible to arrange all the observed $AuCl^{35}$ bands in two systems, which will be called A and B. All observed bands are represented within experimental error by the following formulas. The formulas for $AuCl^{35}$ were obtained directly from the data, and those for $AuCl^{37}$ were then calculated from theory using the appropriate value (see below) of the isotopic coefficient ρ. The equations are given as functions of $n+\frac{1}{2}$, $(n=0, 1, 2 \ldots)$ because this is required by the new quantum mechanics and has also been shown to be necessary experimentally for certain molecules,[3] although not required by the experimental data in the present case.

$$A\begin{cases}\text{AuCl}^{35}\text{: } \nu = 19113.8+312.0(n'+\frac{1}{2})-382.8(n''+\frac{1}{2})-0.70(n'+\frac{1}{2})^2+1.30(n''+\frac{1}{2})^2\\ \text{AuCl}^{37}\text{: } \nu = 19113.8+304.8(n'+\frac{1}{2})-373.9(n''+\frac{1}{2})-0.67(n'+\frac{1}{2})^2+1.24(n''+\frac{1}{2})^2\end{cases}$$

$$B\begin{cases}\text{AuCl}^{35}\text{: } \nu = 19238.3+316.3(n'+\frac{1}{2})-382.8(n''+\frac{1}{2})-1.45(n'+\frac{1}{2})^2+1.30(n''+\frac{1}{2})^2\\ \text{AuCl}^{37}\text{: } \nu = 19238.3+309.0(n'+\frac{1}{2})-373.9(n''+\frac{1}{2})-1.38(n'+\frac{1}{2})^2+1.24(n''+\frac{1}{2})^2\end{cases}$$

Isotope Effect

The theoretical isotopic coefficient[4] ρ has the value 0.9768 for $AuCl^{37}$ as compared with $AuCl^{35}$. As already noted above, the equations for the $AuCl^{37}$ heads were calculated from those experimentally determined for

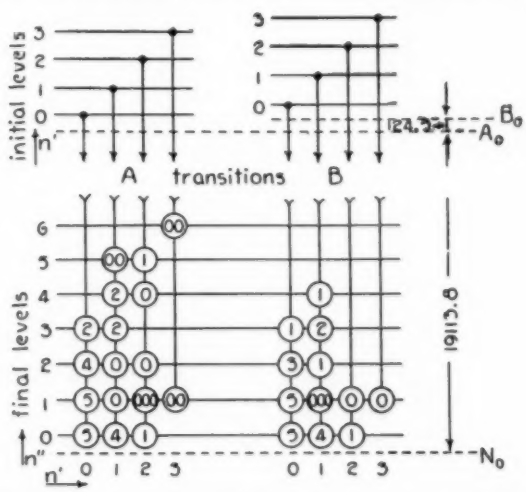

Fig. 2. Energy-levels and transitions in AuCl. N_0 represents the final (normal), A_0 and B_0 the excited electronic levels. Vibrational levels are drawn to scale (indicated by the separation of A_0 and B_0).

$AuCl^{35}$. The agreement of the observed $AuCl^{37}$ heads with these equations (Tables I and II) confirms the identification of the emitting molecule as AuCl. The value of ρ for the isotopes (197, 199) of gold is 0.9992 for AuCl, too near unity to permit their resolution with the dispersion here employed.

[3] R. S. Mulliken, Phys. Rev. **25**, 259 (1925); F. A. Jenkins, Proc. Nat. Acad. Sci. **13**, 496 (1927).

[4] R. S. Mulliken, Phys. Rev. **25**, 119 (1925).

Energy Levels

The identity of the coefficients of the terms in n'' for systems A and B shows that these have the same final electronic state. This is presumably the normal state of the AuCl molecule.

The energy-level diagram (Fig. 2) shows the observed electronic and vibrational levels as determined by this analysis for AuCl.[35]

Intensities

Relative intensities in each system are indicated by numbers in the small circles of Fig. 2. In each system the maximum is near the origin, and the intensity varies in accordance with the theory proposed by Condon.[5] In both the AuCl systems the ratio of final to initial vibrational frequencies is rather far from unity. As is predicted by Condon's theory for such a case, a curve drawn through the strong bands on the $n'n''$ diagram would have a rather wide-open parabolic form.

An attempt was made to excite the bromide and also the iodide of gold by this method, but with no success.

To Professor R. S. Mulliken for his suggestions and guidance during the course of this work the writer is deeply grateful.

Washington Square College,
New York University.
March, 1928.

[5] E. U. Condon, Phys. Rev. **28**, 1182 (1926).

STARK EFFECT AND SERIES LIMITS[1]

By H. P. Robertson and Jane M. Dewey[2]

Abstract

Energy of conditionally periodic and aperiodic orbits in hydrogen-like atoms under the influence of an external electric field.—It is shown that the energy of a conditionally periodic orbit in a hydrogen-like atom under the influence of a homogeneous external field F must be less than $-(3/2)[eFp_\phi/m^{1/2}]^{2/3}$. Aperiodic orbits of less, as well as of greater, energy than this value can exist, and in one class of these the electron may approach the nucleus within distances comparable with the dimensions of periodic orbits. The lower limit of the energy of these orbits is approximately $-2e(eF)^{1/2}$.

Applications to spectra.—Since the energy of an aperiodic orbit can assume any one of a continuum of values, it is concluded that the line spectrum of such an atom must end at a point on the long wave-length side of the normal series limit, and that the continuous spectrum, arising from transitions involving an aperiodic orbit, may extend even further within the normal series limit. Application to the mean field in actual gases gives the position of the maximum of the continuous spectrum in good agreement with the observed values. Further experiments for checking the theory are described.

THE behavior of a hydrogen-like atom under the influence of an external homogeneous electric field has been discussed, from the standpoint of the older quantum theory, by Epstein,[3] Schwarzschild,[4] Bohr,[5] Lenz[6] and others. The aspects of the problem which they have considered relate, however, to states of the atom so far from ionization that the theory of perturbations can be validly applied. It is the purpose of the present paper to investigate, also on the Bohr theory, the nature of the mechanically possible orbits of small negative energy, and to discuss the bearing of the results obtained on series limits and continuous atomic spectra.

Orbits in Atom in Homogeneous Field

The motion of an electron in the field of a core of residual charge $+e$ and a homogeneous electric field of strength F is determined by its kinetic energy $\frac{1}{2}mv^2$ and potential energy $-e^2/r+eFz$ where z is the component of its distance r from the nucleus in the direction of the field. In parabolic coordinates (ξ, η, ϕ)[7] defined by

$$x=(\xi\eta)^{1/2}\cos\phi,\quad y=(\xi\eta)^{1/2}\sin\phi,\quad z=\tfrac{1}{2}(\xi-\eta)\ ;\ (\xi,\eta\geqq 0) \tag{1}$$

the Hamiltonian function is

[1] Preliminary report by Dewey and Robertson in Nature 1928, p. 709.
[2] National Research Fellows.
[3] P. S. Epstein, Phys. Zeits. **17**, p. 148 (1916); Ann. d. Physik **50**, p. 489 (1916).
[4] K. Schwarzschild, Berl. Ber. p. 548 (1916).
[5] N. Bohr, "Quantentheorie der Linienspektren", p. 101 (Braunschweig, 1923).
[6] W. Lenz, Zeits. f. Physik **24**, p. 197 (1924).
[7] The notation is essentially that of W. Pauli, Hndbch. d. Physik **23**, p. 130 (Berlin, 1926).

$$H(\xi,\eta,\phi\,;p_\xi,p_\eta,p_\phi)=\frac{1}{2m(\xi+\eta)}\left\{4\xi p_\xi^2+4\eta p_\eta^2+\left(\frac{1}{\xi}+\frac{1}{\eta}\right)p_\phi^2 +meF(\xi^2-\eta^2)-4me^2\right\}$$

and the Hamilton-Jacobi equation

$$H(\xi,\eta,\phi\,;\partial S/\partial\xi,\partial S/\partial\eta,\partial S/\partial\phi)=W \tag{3}$$

is soluble by the method of separation of variables.[8] The momenta are then given by

$$p_\xi=\frac{\partial S}{\partial\xi}=\frac{1}{2\xi}[f(\xi)]^{1/2},\qquad p_\eta=\frac{\partial S}{\partial\eta}=\frac{1}{2\eta}[g(\eta)]^{1/2},\qquad p_\phi=\frac{\partial S}{\partial\phi}=\text{const}. \tag{4}$$

where

$$f(\xi)=-meF\xi^3+2mW\xi^2+2\alpha_1\xi-p_\phi^2,\quad g(\eta)=meF\eta^3+2mW\eta^2+2\alpha_2\eta-p_\phi^2 \tag{5}$$

and α_1, α_2 are constants subject to the relation

$$\alpha_1+\alpha_2=2me^2. \tag{6}$$

The orbits which can be quantized, whose energy W is consequently limited to a discrete set of values, must be *conditionally periodic*. The theory of such orbits requires that each of the functions $f(\xi)$ and $g(\eta)$ then have two non-negative roots between which they are themselves positive (or, in some cases, a multiple root; a coordinate for which this occurs must retain this

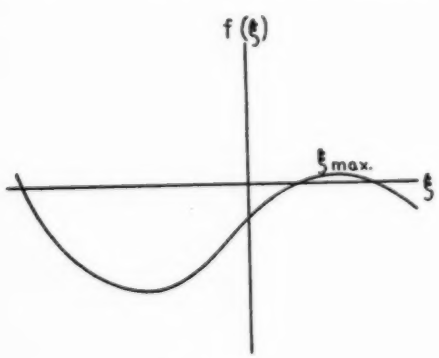

Fig. 1.

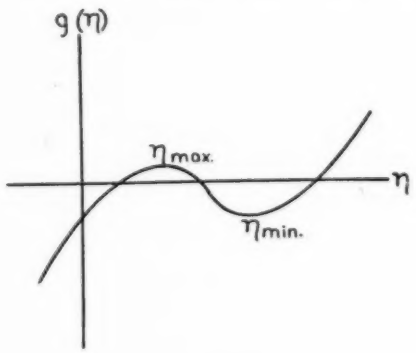

Fig. 2.

constant value throughout the motion). Orbits which do not satisfy these conditions, which we shall for the sake of brevity refer to as *aperiodic*,[9] cannot be quantized, and their energy may assume any of a continuum of values. The present investigation concerns itself primarily with interpreting these conditions in terms of the *mechanically* permissible values of $W<0$,

[8] Strictly speaking, m is the reduced mass $m_{el}m_{nu}/(m_{el}+m_{nu})$ of the electron.

[9] We disregard motions of *limitation*.

and not with the actual determination of the quantized values. With this knowledge of the range of energy allowed in these two types of motion we can predict the nature and position of spectra produced by such an atom, transitions between two quantized states giving rise to a line spectrum and transitions in which one of the states involved is aperiodic to a continuous spectrum.

Conditionally periodic orbits. The conditions mentioned above for orbits of this type require, with regard for the fact that $f(0)=g(0)=-p_\phi^2<0$, that all roots of the cubics $f(\xi)$ and $g(\eta)$ be real and, with the exception of the least root of $f(\xi)$, positive.[10] This can be expressed analytically (cf. Figs. 1 and 2):

$$\xi_{\max} \text{ real and } >0\,; \quad f(\xi_{\max})\geqq 0 \tag{7}$$

$$\eta_{\max} \text{ real and } >0\,; \quad g(\eta_{\max})\geqq 0,\ g(\eta_{\min})<0 \tag{8}$$

where the subscripts max and min indicate that value of the variable for which the corresponding cubic has a maximum and minimum respectively.

We first note that since the sum of the three (positive!) roots of $g(\eta)$ must equal $-2W/eF$, W must be negative:

$$W<0. \tag{9}$$

For simplicity we introduce the notation

$$\begin{aligned} &X=2mW^2/3eF,\ i.e.\ W=-(3eFX/2m)^{1/2}\\ &P=(3/8)(6meF)^{1/2}p_\phi^2,\ B=2me^2 \end{aligned} \tag{10}$$

The extrema of the cubics are then

$$\xi=2/(6meF)^{1/2}\left[\mp(X+\alpha_1)^{1/2}-X^{1/2}\right],\ \eta=2/(6meF)^{1/2}\left[X^{1/2}\mp(X-\alpha_2)^{1/2}\right]. \tag{11}$$

From these, the first conditions of (7) and (8), and the relation (6) the restrictions on α_1 and α_2 are found to be

$$\left.\begin{matrix}0<\\ B-X\leqq\end{matrix}\right\}\alpha_1<B, \qquad 0<\alpha_2\begin{cases}<B\\ \leqq X\end{cases},\quad \alpha_1+\alpha_2=B. \tag{12}$$

Finally, the remaining conditions of (7) and (8) become

$$\begin{aligned} &-\tfrac{1}{2}\alpha_1X^{1/2}+(X+\alpha_1)\left[(X+\alpha_1)^{1/2}-X^{1/2}\right]\geqq P\\ &\tfrac{1}{2}\alpha_2X^{1/2}-(X-\alpha_2)\left[X^{1/2}-(X-\alpha_2)^{1/2}\right]\geqq P\\ &\tfrac{1}{2}\alpha_2X^{1/2}-(X-\alpha_2)\left[X^{1/2}+(X-\alpha_2)^{1/2}\right]<P \end{aligned} \tag{13}$$

These inequalities define the range of W within which the energy of a conditionally periodic orbit must lie.

In unperturbed hydrogen only orbits with negative total energy can be quantized, and this occurs in such a way that there exist (highly excited) orbits whose energies are arbitrarily near zero (ionization). We now ask if

[10] $p_\phi=0$ must be excluded, as in this case the conditionally periodic orbits would approach arbitrarily near to the nucleus. This exclusion is effected automatically in the new quantum mechanics (cf. E. Schroedinger, Ann. d. Physik **80**, p. 463 (1926)).

there exists an analogous upper limit for the energy of quantized orbits in the case under consideration; this will be characterised by the smallest value of X compatible with the above inequalities, so we first investigate the possibility of orbits for which $X<B$ (the least restrictive case). (12) then restricts α_1 to values not greater than X, and from the second inequality of (13)

$$\tfrac{1}{2}\alpha_1 X^{1/2}\geqq P,\ i.e.\ X^{1/2}\geqq 2P/\alpha_2\geqq 2P/X$$

whence
$$X\geqq(2P)^{2/3} \tag{14}$$

Furthermore, although orbits with energy corresponding to the equality sign in (14) can be shown to be either unstable or constitute a motion of limitation, the inequalities (13) can be satisfied by conditionally periodic orbits whose energy is less but arbitrarily near this limiting value provided

$$P<4B^{3/2}/27 \quad [11] \tag{15}$$

We may consequently state: *There exist no quantizable orbits whose total energy is greater than*

$$-\frac{3}{2}\left(\frac{eFp_\phi}{m^{1/2}}\right)^{2/3} \quad [12] \tag{14'}$$

and only in case
$$|p_\phi|<\frac{8}{9}\left(\frac{me^3}{(3eF)^{1/2}}\right)^{1/2} \tag{15'}$$

can there exist quantizable orbits with energy in the neighborhood of (14'). The complete discussion of cases in which F or $|p_\phi|$ is so large that the inequality (15) is not satisfied is more complicated; it will be found expedient in any given case to apply the method of successive approximation to the inequalities (13) in order to obtain the limitation imposed on the energy. In any case the energy must be so small that (14) and

$$X>(2P/B)^2,\ i.e.\ W<-9Fp_\phi^2/8me \tag{16}$$

(which follows from the fact that $\alpha_2<B$ and the inequality preceeding (14)) are satisfied; the larger of these two lower bounds for X may be taken as a starting point for the method. However (15) is satisfied in the applications which we wish to consider, and consequently the statement above is sufficient for our purposes.

As a consequence of the above and the fact that the lower quantum states suffer only the ordinary Stark effect splitting, the short wave-length limit of the series produced by transitions from or to one of these lower states

[11] This can be proven by noting that if the last two inequalities of (13) are satisfied by values X', α_2' of X, α_2, then they are also satisfied by $X'+s$, $\alpha_2'+\frac{1}{2}s$, where s is any positive quantity.

[12] A simple derivation of the somewhat weaker condition $W<-\frac{1}{2}18^{1/3}(eFp_\phi/m^{1/2})^{2/3}$ can be obtained from the remark above (9) that the sum of the three roots of $g(\eta)$ is $-2W/eF$, together with the fact that each root is certainly greater than p_ϕ^2/α_2, the intercept on the η-axis of the tangent to $g(\eta)$ at $\eta=0$ (cf. Fig. 1). For from (12) $\alpha_2<B=2mW^2/3eF$, whence $-2W/eF>3p_\phi^2/\alpha_2>9p_\phi^2eF/2mW^2$ and the desired inequality follows immediately.

will be displaced toward smaller frequencies by an amount corresponding approximately to (14′). In accordance with the views of Bohr and others concerning continuous atomic spectra, we should expect that a continuous spectrum would extend from this displaced limit toward shorter wavelengths.

Aperiodic orbits. According to the above an orbit whose energy is greater than (14′) will be aperiodic, but it does not follow that orbits of less energy are necessarily conditionally periodic. Returning to equations (4) it is seen that since $g(\eta)$ is a cubic in which the coefficient of η^3 is positive there exist aperiodic orbits, for which η is greater than the largest root of $g(\eta)$, corresponding to any choice of W and α_1 which satisfy conditions (7) (for if these were not satisfied $f(\xi)$ would be negative for all positive ξ and p_ξ would consequently be imaginary). In general, however, these orbits are at a comparatively large distance from the nucleus and may be considered as representing the motion of an essentially free electron in the electric field—as, for example, the orbits for which η is greater than the largest root of $g(\eta)$ in Fig. 2.

Restricting ourselves to aperiodic orbits whose total energy is negative, there does exist a class of such orbits in which the electron may approach the nucleus within a distance comparable with those of the lower quantized orbits. They are characterised by the fact that for them $g(\eta)$ has but one real root and is positive at the point of inflection. These orbits are of two kinds,

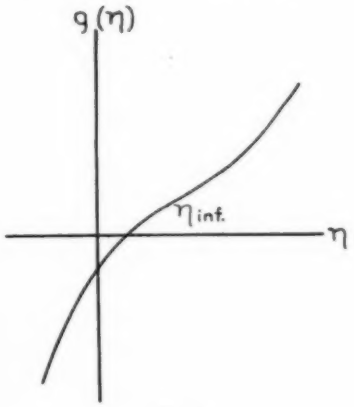

Fig. 3.

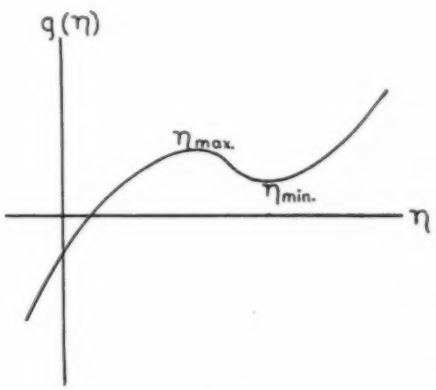

Fig. 4.

(a) those for which $g(\eta)$ has no extrema (Fig. 3), and (b) those in which there exist real extrema at which $g(\eta)$ is positive (Fig.4); in either case the conditions (7) on $f(\xi)$ must be satisfied. The conditions for (a) may be written

$$\begin{gathered} 0<\alpha_1 \leqq B-X,\ X \leqq \alpha_2 < B, \\ -\tfrac{1}{2}\alpha_1 X^{1/2}+(X+\alpha_1)\left[(X+\alpha_1)^{1/2}-X^{1/2}\right] \geqq P, \end{gathered} \tag{17}$$

and for (b)

$$\begin{gathered} \left.\begin{matrix} 0< \\ B-X \leqq \end{matrix}\right\} \alpha_1 < B,\ 0<\alpha_2 \begin{cases} <B \\ \leqq X \end{cases}, \\ -\tfrac{1}{2}\alpha_1 X^{1/2}+(X+\alpha_1)\left[(X+\alpha_1)^{1/2}-X^{1/2}\right] \geqq P, \\ \tfrac{1}{2}\alpha_2 X^{1/2}-(X-\alpha_2)\left[(X-\alpha_2)^{1/2}+X^{1/2}\right] > P. \end{gathered} \tag{18}$$

We are now interested in determining the largest X, *i.e.* the smallest energy, compatible with the inequalities (17) or (18); from this the maximum extension of the continuous spectrum *inside* the normal series limit, corresponding to transitions between a lower quantum state and these nearer orbits (*i.e.* ionization or capture of an electron by the ion), can be determined. Again, in the applications considered later an inequality similar to (15) holds, which we write

$$\epsilon^2 = P/B^{3/2} << 1 \tag{19}$$

Examination of the third inequality of (17) shows that for orbits of type (a) X must be less than B by a term of order $B\epsilon$; the largest value of X compatible with this inequality is found by expansion to be, within terms of order $B\epsilon^2$,

$$X = B(1 - 2(6)^{1/2}\epsilon/3). \tag{20}$$

On the other hand, orbits of this type can be found for which X is arbitrarily small.

The inequalities (18) require that for orbits of type (b) X be greater than the two lower bounds $(2P)^{2/3}$ and $(2P/B)^2$ found in the investigation of periodic orbits. The left hand side of the last inequality of (18) is a monotonically decreasing function of X with a root at $X = 4\alpha_2/3$; X must consequently be less than $4B/3$. Examination of the behavior of this inequality when α_2 and X are in the neighborhood of B and $4\alpha_2/3$ respectively gives as the maximum of X

$$X = (4B/3)(1 - 4(3)^{1/4}\epsilon/3) \tag{21}$$

We thus arrive at the conclusion that there can exist in addition to aperiodic orbits with positive energy certain others, having small perihelion distances, whose energies are negative and range down to approximately

$$W = -2e(eF)^{1/2}[1 - 2(3)^{1/4}\epsilon/3] \tag{21'}$$

Transitions involving a lower quantum state and these orbits will give rise to a continuous spectrum which extends *within* the normal series limit a distance corresponding to (21'). Superposed on a portion of this continuous spectrum there may occur lines arising from transitions involving periodic orbits of comparable energy. A discussion of the relative probability of these various transitions would necessitate applying the new quantum mechanics, and would carry us beyond the scope of the present paper.

Spectral Applications

That only an isolated atom in the absence of any field can have spectral terms of energy arbitrarily close to zero has been known since the earliest days of the quantum theory and is in accord with observations on spectra. Bohr[13] first showed this from spacial considerations and Franck[14] pointed

[13] Bohr, Phil. Mag. **26**, 9 (1913).

[14] Franck, Zeits. f. Physik **1**, 2 (1920).

out that the electric field of nearby atoms and ions must be the controlling factor. Oldenberg[15] has suggested that a Stark effect displacement of the series limit in the direction of lesser energy would explain the observation of continuous spectra to the red of the normal limit. We see the effect in the small number of lines observed in turbulent discharges and the large number observed in absorption in diffuse vapors.[16] Also it has been observed that stars with sharp spectral lines show maxima of continuous absorption nearer the normal limit than do those with broad spectral lines.[17]

The quantitative application of conditions (14′), (15′) and (21′) to an actual gas is at best a rough approximation, for the fields in a gas arise from the presence of ions and from the electric moments of the atoms themselves and are unhomogeneous. In the case of the strongest mean fields which we shall consider, however, (8 e.s.u. per cm.) the mean distance of the charged particles from each other is of the order of 10^{-5} cm and the radius of the largest periodic orbit that can exist is of the order of 10^{-6} cm; the variation in the field is therefore in general only a fraction of its magnitude. The variation due to the motion of the charges is small compared to the variation in space for stationary charges as long as the velocity of the electron which forms part of the atom is large compared to that of the charges which set up the external field. Holtsmark[18] calculated the width of spectral lines from the Stark effect displacements for homogeneous fields and obtained good agreement with observed widths. The approximation is probably better in the cases he considers than near the series limit because of the smaller size of the orbits.

To determine of the displacement of the limit to be expected the formula are given in numerical form. From (14′) $W<-9.9\times10^{-16}(MF)^{2/3}$ ergs, where M is the "equatorial" (magnetic) quantum number and the field F is expressed in electrostatic units per centimeter, or

$$\nu>5.2(MF)^{2/3}\text{cm}^{-1} \qquad (14'')$$

Where ν is the term frequency of the last mechanically possible periodic orbit. For the aperiodic orbits of smallest energy we obtain

$$\nu<(109F^{1/2}-0.8F^{3/4}\,|\,M\,|)\text{cm}^{-1} \qquad (21'')$$

We cannot expect to observe all the lines allowed by condition (14″) for they may be too weak to be photographed, and for this reason it is not useful for quantitative application. All we can say is that no lines have been observed which it would exclude. We can apply condition (21″) to the observed continuous atomic spectrum of hydrogen.

In laboratory sources, hydrogen gives a continuous spectrum which extends over the entire visible and ultra-violet region and may be ascribed to

[15] Oldenberg, Zeits. f. Physik **41**, 1 (1927), see also Saha, Nature, **114**, 155 (1924).
[16] Wood, Astrophys. J. **29**, 97 (1909); **43**, 73 (1916).
[17] See, for instance, Payne, Stellar Atmospheres, Cambridge, Mass., 1925, p. 43.
[18] Holtsmark, Ann. d. Physik **58**, 577 (1919); Phys. Zeits. **25**, (1924).

the molecule. In the stars, however, because of their high temperatures, very few molecules can be present and we can assign the continuous spectrum observed near the limit of the Balmer series to the atom. Wright[19] attempted to explain the appearance of the portion of the continuous spectrum within the normal series limit by assuming that there exists a last quantized orbit, beyond which the electron becomes free and has less energy. This is, however, impossible from energetic considerations; his hypothesis neglected the potential energy of the quantized orbits. Wright's theory was extended by Crew and Hulburt[20] and applied to their measurements on the continuous spectrum of a hydrogen discharge tube. In their form of the theory it is not clear from what source the electron obtains the energy necessary to remove it to any distance from the nucleus when the atom is ionized by light of a frequency less than the limiting frequency. According to the ideas presented here this energy is taken up from the electric field or, in the case of stray fields of ions, from the kinetic energy of the ion or ions in whose field the atom lies. As this energy is small (0.04 volts at most in our applications) it will in general be available; if it is not, the ion and electron will recombine with emission of light of the same or longer wave length than that absorbed. The continuous spectrum of hydrogen has been discussed by various authors and complete bibliographies are given by Anderson[21] and by Herzberg.[22]

The most recent and extensive data on the continuous atomic spectrum of hydrogen are those of Yü[23] who measured the absorption as a function of wave length in the neighborhood of the limit of the Balmer series for a large number of stars. Hartmann[24] also gives photometric measurements on a few stars. According to these authors the maximum of absorption in many class A and class B stars occurs at 3700A and absorption is appreciable 100 to 150A to the red of this wave length. Russell and Stewart[25] and Eddington[26] estimate the mean field in the sun to be 6 e.s.u. per centimeter. Since according to Payne[27] the ion and electron concentrations in these stars are of the same order as in the sun, we shall take this estimate for these stars also. In α cygni, a giant star, as well as in the chromosphere[28] and the nebula N. G. C. 1499,[29] the limit of continuous absorption is close to the normal limit, as we should expect from the rarified condition of these spectral sources. Herzberg[30] has recently succeeded in obtaining the continuous spectrum of atomic hydrogen distinct from the molecular spectrum in an electrodeless ring discharge. On the reproductions of plates which

[19] Wright, Nature, **109**, 810 (1922).
[20] Crew and Hulburt, Phys. Rev. **28**, 936 (1926).
[21] Anderson, Zeits. f. Physik **38**, 530 (1926).
[22] Herzberg, Ann. d. Physik **34**, 555 (1927); Phys. Zeits. **28**, 727 (1927).
[23] Yü, Lick Bull, **12**, 104 (1926).
[24] Hartmann, Phys. Zeits. **18**, 429 (1917).
[25] Russell and Stewart, Astrophys J. **59**, 197 (1924).
[26] Eddington, The Internal Constitution of the Stars, Oxford 1926, p. 356.
[27] Payne, loc. cit. pages 110 and 173.
[28] Evershed, Phil. Trans. **197**, 381 (1901).
[29] Hubble, Pub. A. S. P. **32**, 155 (1920).
[30] Herzberg, loc. cit.

accompany his article the continuous spectrum overlaps the lines to about 300 cm^{-1} within the limit and the last lines appear 200 cm^{-1} within the limit. There is now way of estimating the field in an electrodeless discharge. It is probably appreciable as the continuous spectra will not be emitted with observable intensity unless the ion concentration is large. Balasse[31] reports the appearance of forbidden lines in a similar discharge in caesium.

Since any atom becomes hydrogen-like as one of its electrons is removed to higher quantum states we can apply these considerations to any continuous atomic spectrum. Paschen[32] observed three continuous spectra in helium using a discharge of high electron concentration. He reports that the spectra appearing near the $2s$ and $2p$ limit extend 275 cm^{-1} to the red of the normal limit. The maximum of the $2s$ spectrum appears on the reproduction to lie about 190 cm^{-1} to the red of the limit. Mohler[33] has recently made photometric measurements on the continuous spectra of caesium and observed maxima in the intensity 250 and 300 cm^{-1} to the red of the limits $2P$ and $2D$ respectively, with an appreciable intensity extending at least 1500 cm^{-1} to the red in the later case; the $2P$ spectrum overlaps the $2D$ so that it is not possible to judge its extension to the red of the maximum. In tubes similar to the one in which he observed this emission he has measured an ion concentration of 10^{14} ions per cubic centimeter.[34] From this ion concentration one obtains by the formula of Holtsmark[17] a field of 8 e.s.u. per centimeter. Table I collects these data and gives the limit, calculated from

TABLE I

Element	Limit	Authority	Field (e.s.u.)	Distance from Normal Limit (cm^{-1}) Calc. Limit	Obs. Maximum	Obs. Limit
H	Balmer	Yü	6	270	350	1200
H	Balmer	Herzberg			200	300
He	2s	Paschen	3	175	190	275
He	2p	Paschen	3	175		275
Cs	2P	Mohler	8	310	250	
Cs	2D	Mohler	8	310	300	>1500

formula (21″), of the continuous spectrum which would be emitted were all the atoms exposed to a homogeneous field of the magnitude of the mean stray field in the gas. A continuous spectrum emitted in the absence of field would have a maximum intensity just to the violet of the normal limit. If we assume that the intensity in a homogeneous field would be distributed in somewhat the same way and consider the spectrum emitted in a gas as the sum of spectra emitted in fields distributed around the mean, the maximum intensity will lie just to the violet of this new calculated limit, since most of the atoms are exposed to fields close to the mean. The extension of the

[31] Balasse, C. R. **184**, 1002, (1927).

[32] Paschen Berl. Sitzb. 1926, p. 135.

[33] Mohler, Phys. Rev. **31**, 187 (1928).

[34] Reported at the meeting of the American Physical Society, Feb. 25, 1928 in New York City.

spectrum to the red of this limit is to be expected since at any given time a large number of atoms are exposed to fields larger than the mean.

The excellence of the agreement in all but the first case must be regarded as fortuitous as, even if the theory were strictly applicable, the fields are not estimated with accuracy. In addition the observed continuous spectrum is the sum of the true continuous spectrum and of the line spectrum which is spread over the whole background by the unhomogeneous field. In the reproductions of Paschen's and of Herzberg's plates and on a plate Dr. Mohler was kind enough to send us the continuous spectrum overlaps a number of apparently sharp lines of considerable intensity so that it is unlikely that very much of the continuous spectrum arises from the spreading out of the lines. We must also consider the question of probability: it is not necessarily true that the maximum probability of transition occurs for energies very close to the displaced limit; it may be that this probability is a maximum for some frequency greater than this. Even for frequencies to the violet of the normal limit and neglecting the effect of the field on changing the selection principle we cannot expect the observed variation of intensity with wave-length to conform to that predicted by the theory for an unperturbed atom,[35] for, because the atoms are exposed to varying fields, a given frequency is not associated with any given kinetic energy of the free electron but may be emitted or absorbed in various types of transitions giving the same energy. These difficulties must be introduced for all emission spectra and all absorption spectra not associated with the normal state of the atom, except as we observe them in nebulae or other rarified sources of enormous volume, since in a laboratory source a large ion concentration is necessary to obtain observable intensity.

Experiments are under way to investigate the continuous spectrum of helium in a tube in which measurements of electron concentration can be made. It is also planned to investigate the absorption spectrum of rarified caesium vapor in a homogeneous electric field, so that a direct check on the theory can be obtained.

The authors wish to express their appreciation for the interest which Professor K. T. Compton has shown during the course of the work, and to thank Dr. Mohler for data sent them in advance of publication.

PALMER PHYSICAL LABORATORY,
PRINCETON, N. J.,
March 6, 1928.

[35] Kramers, Phil. Mag. **46**, 386 (1923); Oppenheimer, Camb. Phil. Soc. **23**, 422 (1926); Zeits. f. Phys. **41**, 268 (1927).

THE RESONANCE LINE OF THE IODINE ATOM AND THE OPTICAL DISSOCIATION OF IODINE MOLECULES

By Louis A. Turner

Abstract

The resonance line of the iodine atom is most probably that of wave-length 1830.4A, corresponding to a resonance potential of 6.75 volts. Light of that wave-length is absorbed by a cell containing iodine vapor more strongly when it is illuminated by concentrated light from a carbon arc than when it is not so illuminated. The increased absorption is attributed to iodine atoms produced by the illumination, in accord with Franck's theory of optical dissociation.

THE absorption spectrum of iodine in the visible region consists of sequences of bands which are closer together on the side of shorter wave-lengths and converge to a limit at 4995A, beyond which there is a region of continuous absorption. Franck[1] suggested that absorption of light in this region results in the dissociation of I_2 molecules into separate I atoms, one in the normal state, the other in a metastable excited state. This theory was supported by the experiments of Dymond[2] who found that when light of wave-length longer than 4995 was absorbed fluorescence light was re-emitted but that when light of wave-lengths in this continuous region was absorbed there was no fluorescence, as would be the case if the two atoms were separated. Kuhn[3] investigated the absorption spectra of bromine and chlorine, finding them to be of the same sort, and showed that the heat of dissociation for each substance as calculated by Franck's theory agreed with that determined by thermal methods, within the experimental accuracy of the latter. Thus, there could be very little doubt as to the correctness of Franck's theory. Nevertheless, it seemed that it might be of interest to demonstrate the dissocation by an experiment which would indicate the presence of the iodine atoms directly. A consideration of the probable absorption spectrum of the iodine atom showed that the absorption of light of the proper wave-length could be used as a distinctive and delicate test for the presence of the atoms.

The Resonance Line of Iodine

A line spectrum of iodine has not been observed in absorption nor has the spectrum of emission lines been completely analyzed, but it is possible to conclude from very general considerations that light of the wave-lengths of certain of these lines must be absorbed by the normal atoms. According to Hund's theory, the normal electronic configuration of a halogen atom

[1] J. Franck, Trans. Faraday Soc. **21**, part 3 (1925); and Zeits. f. Phys. Chem. **120**, 144 (1926).

[2] E. G. Dymond, Zeits. f. Physik **34**, 553 (1925).

[3] H. Kuhn, Zeits. f. Physik **39**, 77 (1926).

gives an inverted ^2P term. A recurring frequency difference between lines of the arc spectrum of iodine in the Schumann region has been found,[4] and is most probably the frequency difference between these two levels of the P term. The term being inverted, the j value of the lower and normal level is 3/2, that of the upper is 1/2. Any upper level which combines with these will, if its j is 3/2 or 1/2, give two lines having the $\Delta\nu$ characteristic of the lower levels. If its j is 5/2 it can combine only with the lower level, the j of which is 3/2. A level with j equal to 7/2 or more can combine with neither of the low levels. The line of shorter wave-length of each pair having the frequency difference of the ^2P term would therefore be absorbed by normal atoms. Further, any line in the region of the spectrum of lines involving jumps to the low ^2P levels which is single (i.e., has no companion with a $\Delta\nu$ characteristic of the low ^2P levels) must be connected with jumps from a higher state for which $j=5/2$ to the normal level for which $j=3/2$, and light of that wave-length must be absorbable by atoms in the normal state.

The iodine line of this latter sort of longest wave-length is the exceedingly strong 1830.4 line. It is, most probably, the $a^2P_{3/2}-k^4P'_{5/2}$ line[5] which is predicted by Hund's theory to be the single line of longest wave-length, as follows. The low ^2P term comes from the p^5 configuration. The next higher terms must come from the p^4s configuration which gives $^4P'$, $^2P'$, ^2S, and ^2D terms. Of these the $^4P'$ and the $^2P'$ should be much the lowest, the $^4P'$, somewhat lower than the $^2P'$, and both inverted. These predictions have been fulfilled in the spectra of Ne^+ and A^+, recently analyzed.[6] The lowest level of all of this group is the $^4P'_{5/2}$ which, combining with $^2P_{3/2}$, most probably gives the 1830.4 line. The other strong lines of longer wave-lengths, viz., 2062.1, 1876.4, 1844.5, are emitted by transitions to the $^2P_{1/2}$ level. 1830.4 is therefore the resonance line of the atom, corresponding to a critical potential of 6.75 volts. This value is in better agreement with Kondratjew[7] and Leipunsky's measured value of 6.5 volts than the previously suggested value of 6.92 volts, which is the energy of excitation of the upper level involved in the emission of the strong 2062.1 and 1782.9 lines.

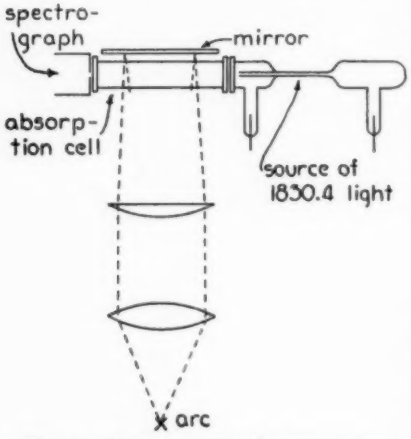

Fig. 1. Arrangement of apparatus.

The Optical Dissociation of Iodine

Light of a wave-length of 1830.4A should therefore be absorbed by iodine atoms and can be used to detect their presence. The apparatus was arranged as shown in Fig. 1. The source of the 1830.4 light was a discharge tube of the form indicated in the figure, with a quartz win-

[4] L. A. Turner, Phys. Rev. **27**, 397 (1926).
[5] Bowen's notation. I. S. Bowen, Phys. Rev. **29**, 231 (1927).
[6] H. N. Russel, K. T. Compton and J. C. Boyce, Proc. Nat. Acad. Sci. **14**, 280, 1928.
[7] A. Kondratjew, and A. Leipunsky, Zeits. f. Physik **44**, 708, 1927.

dow, containing iodine, and excited by a small transformer. The absorption cell was of glass with quartz windows at the ends. It was connected to the pumps through liquid air traps. An appendix containing iodine was usually left at room temperature so that the maximum vapor pressure of iodine was 0.2 mm. Light from a strong carbon arc could be concentrated upon it by lenses, the second of which gave an astigmatic bundle focussed in a line along the axis of the cell. The spectrograph was a small Hilger quartz spectrograph which had been readjusted for work with light of these shorter wave-lengths. Commercial nitrogen from a tank was flowed through it continually so as to eliminate the absorption by the oxygen of the air in the region of the shorter wave-lengths. Schumann plates were used.

It was found that other things being equal, the intensity of the 1830.4 line on the plate was cut down decidedly by the illumination of the iodine in the absorption cell by light from the arc. The 1844.5 and 2062.1 lines were not so absorbed, showing that the $^2P_{1/2}$ metastable atoms produced in the optical dissociation must quickly revert to the normal $^2P_{3/2}$ state. One would expect that they would do so by collisions of the second kind with iodine molecules. This absorption produced by illumination was superposed upon a considerable absorption by molecular iodine in this region. In order to show that the increase of absorption produced by illuminating the tube is absorption of a very narrow region of the spectrum by atoms, rather than an increase of absorption in the whole region, light from a Geissler tube containing CO_2 was passed through the cell instead of that from the tube containing iodine. This tube gave, with great intensity, the CO bands found by Schumann. One of these has its head on the side of shorter wave-lengths at 1830.2A and is wide enough to serve as a continuous background over a range of wave-lengths including that of the iodine line. Indications of an absorption line produced by the illumination of the cell were obtained but not with sufficient regularity and reliability to be at all certain. This is not surprising since the absorption of the line from the iodine tube, of just the right wave-length, was not great, although quite definite. The experiments with the CO band gave no indication, however, of an increase in the general absorption in the neighborhood of the 1830.4 line. The conclusion is that the absorption produced by the illumination of the cell is absorption of a very narrow region at 1830.4A, exactly that predicted for iodine atoms, and therefore an indication of the production of these atoms by the light.

The results of the experiment are thus in agreement with the theory of the optical dissociation of iodine, and with the conclusion that the 1830.4 line of the atom is the resonance line. It indicates the usefulness of this optical method for detecting small quantities of iodine atoms.

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THE ZEEMAN PATTERN OF THE HYPERFINE STRUCTURE LINES OF THE RESONANCE LINE OF MERCURY*

By Walter A. MacNair

Abstract

The Zeeman pattern of each of the five hyperfine structure lines of λ2537 ($1^1S_0-2^3P_1$), the resonance line of mercury, has been obtained in fields from 0 to 7 kilogausses. With certain very significant exceptions each one forms a 3/2 normal Zeeman triplet, and is independent of its neighbors, that is, no Paschen-Back effect appears. The parallel branch of one of the five lines actually shifts its position with changes in the field strength. Each one of the five lines has two 3/2 normal perpendicular branches. In addition three of them have one or two extra perpendicular components. Attention is called to the relations between these results and experiments on the *polarization of mercury resonance radiation*. One is warned against any theoretical explanation of the latter phenomena until more is known of the hyperfine structure of the energy levels of mercury. A quartz Lummer-Gehrcke plate was used for the analysis. One rather unusual method of employing it is described.

THIS research was undertaken about a year ago with the hope that the results of it would prove helpful in disclosing the origin of the hyperfine structure of spectral lines. Now that the work is completed, however, it appears that the Zeeman patterns of the the five hyperfine structure lines of λ2537 are so anomalous that they lead one to no definite method of attack on the general problem. Also in the meantime, the hyperfine structures of certain neon lines have been laid to isotopes[1] and those of bismuth lines to an angular momentum of the nucleus.[2] In view of the results of Ellett and myself,[3] which show that in resonance radiation of mercury excited with polarized light, some of the hyperfine structure lines are one hundred percent polarized and some not, the immediate value of the present work seems to lie in its direct connection with resonance radiation phenomena.

Experimental Method

The success of the work depended upon finding a mercury arc which would give narrow hyperfine structure lines while operating in magnetic fields up to 7 kilogausses. A small quartz vacuum arc, of the usual type, completely submerged in water running through a quartz water jacket, served the purpose fairly well up to one kilogauss. In higher fields the hyperfine structure lines began to show considerable broadening, due to the increased current density which results when the discharge is pressed against

* Publication approved by the Director of the Bureau of Standards of the U. S. Department of Commerce.

[1] Hansen, Naturwiss. **15**, 163 (1927).

[2] Goudsmit and Back, Zeits. f. Physik **43**, 321 (1927).

[3] Ellett and MacNair, Phys. Rev. **31**, 180 (1928).

the side of the tube. For use in stronger fields a transformer-operated discharge tube of simple construction filled with a mixture of helium and mercury vapor was found satisfactory. Two nickel-wire coil-electrodes held on tungsten were sealed into a quartz tube of 8 mm inside diameter. A bent side arm contained a drop of mercury and served conveniently for evacuating the tube. The arc-tubes were prepared by baking out while on the pumps, distilling in a drop of mercury after cooling, then admitting the desired amount of helium which was partially purified by passage through charcoal at liquid air temperature. They were then sealed off and ready for use.

To minimize the reversal of λ2537 the mercury well was held at 10°C or below. The pressures of helium which are usable have wide limits. The hyperfine structure pattern of λ2537 begins to become appreciably less distinct with helium pressures of 40 mm, which sets the upper limit. Helium pressures from 8 to 30 mm were actually used although most of the observations were made with 25 mm pressure. Arcs of this sort gave excellent results up to 7 kilogausses, the maximum available, with no sign of failure.

Since we know nothing of the origin of hyperfine structure in mercury, a theoretical objection might be raised to using radiation from a mixture of helium and mercury for the study of the problem in hand. A discussion of this question will be deferred to a later section.

A quartz Lummer-Gehrcke plate of 4.24 mm thickness (two of which were available) is very appropriate for the study of the hyperfine structure of λ2537 because the total width of the ordinary pattern of this line is about 47 mA while the distance between orders of the interferometer is about 52 mA. Consequently each order appears by itself uncomplicated by the overlapping of adjacent orders, a circumstance frequently met with in the study of the structure of lines, especially those of mercury. From the notation of this line, $1^1S_0 - 2^3P_1$, we should expect its Zeeman pattern to be a 3/2 normal triplet and, if each hyperfine structure line forms a triplet independently of the others with no Paschen-Back effect among them, we would observe each of the five[4] well known lines to split into three. To interpret correctly a Lummer-Gehrcke plate photograph of the resulting 15 components would be impossible. Consequently it was necessary to devise some method whereby the large number of expected components could be photographed a few at a time. This was accomplished in the following way.

The parallel components can be separated from the others simply by observing the light polarized parallel and emitted perpendicular to the magnetic field. The perpendicular components can be divided into two groups because of the circumstance that those which increase in wave-length with increase in magnetic field strength are circularly polarized in one sense, and those which decrease are circularly polarized in the opposite sense. These groups were separated by observing the light along the magnetic field through a small hole in one pole piece, passing it through a quarter-wave plate and

[4] Wood, Phil. Mag. **50**, 761 (1925).

Wollaston prism, appropriately set, and thence to the Lummer-Gehrcke plate. With the apparatus adjusted to transmit the right-handed circularly polarized components, through the interferometer to the photographic plate, one observed the long wave-length set with the magnetic field in one direction and the short wave-length set with the field in the opposite direction.

The large electromagnet used to produce the fields has pole pieces which are 10 by 15 cms on the faces and separated by an air gap of 3 cms. It is capable of producing fields up to 7 kilogausses which are uniform to 0.1 percent throughout a volume much larger than that actually used. The observations of the parallel components were made with plain unbored pole pieces and the calibration curve of the magnet was checked with a flip coil after they were complete. One pole piece was then bored with a 1 cm hole through which the observations of the perpendicular components were made. In this latter case the arc-tube was constructed so that it lay against the face of the unbored pole piece. After these observations the calibration curve of the magnet was again checked, with a small flip coil placed so that it would measure the field at the place from which the light had been taken. It is significant that there was no essential difference in the magnitude of the fields obtained before and after boring the pole piece.

The arrangement of apparatus for the study of the parallel components was similar to that employed earlier.[5] In the present case, however, the light taken from the arc in a direction perpendicular to the magnetic field was focussed by means of a fused quartz lens, screened by a vertical slit 1 cm wide, onto the prism of the Lummer-Gehrcke plate. A Wollaston prism set immediately in front of the plate separated the light polarized parallel to the magnetic field (horizontally polarized, becoming the extraordinary ray in the quartz plate) from that polarized perpendicularly. The former beam was focussed by a quartz-fluorite achromatic lens of 25 cms focus onto the slit of an Hilger E2 quartz spectrograph. Fortunately there was available a fused quartz lens of such quality that a 1 cm strip through the center could be selected which was unusually free from strains. Consequently we could be certain that it would not intermix the parallel and perpendicular components of the Zeeman pattern.

For the study of the perpendicular components the arrangement of apparatus, to begin with, was much the same, except that the light from the arc was taken parallel to the magnetic field and passed through a Soleil-Babinet compensator set as a quarter-wave plate for $\lambda 2537$ and mounted in front of the fused quartz lens. One set of circularly polarized components was thus changed to plane horizontally polarized light and the other set to vertically polarized. The hyperfine structure pattern of the former set was then focussed onto the slit of the spectroscope, as usual. The angle of illumination is cut down to a cone of about one degree by the hole in the pole piece, the 1 cm opening in the compensator, and the small aperture of the interferometer plate. Consequently one can obtain at one

[5] MacNair, Phil. Mag. **2**, 613 (1926).

exposure only the structures of lines which lie in a limited spectral region. For instance when the adjustments are made to obtain λ2537 to advantage, light of all wave-lengths longer than 2700A is emitted from the interferometer at angles of emergence less than 88° and do not reach the slit of the spectroscope, while light of wave-lengths shorter than 2200A is totally reflected at the surfaces of the quartz plate. It fortunately happens that 2537 is by far the most intense line in the region from 2700 to 2200A so that it is the only line which appears on the spectrogram. We can then dispense with the spectrograph and put the photographic plate where the slit was, and record the structure directly. This allows a very convenient arrangement of apparatus, for the Wollaston prism, interferometer plate, lens, and plate holder were mounted on an I-beam. The whole was placed in a cork house which reduced the temperature variation during one exposure to a few hundreths of a degree.[6] In this arrangement it was found convenient to use a crystalline quartz lens of 50 cms focus to form the image of the hyperfine structure pattern on the photographic plate.

In order to be certain that the integrated effect of a number of weak lines in the neighborhood of 2537A was not affecting the photographic plate, two exposures were compared, both made with the arc in zero field. The first was taken without and the second with a quartz cell containing mercury vapor in the light path. In the former case the plate developed a dense image while in the latter it was unaffected. Since normal mercury vapor absorbs the light we are photographing we conclude it is all of wave-length 2537A.

In all cases the patterns from both sides of the Lummer-Gehrcke plate were photographed. This allowed the relative positions of the lines to be computed by the method described by McLennan and McLeod[7] from the measurements made with a comparator.

A number of the plates were photometered on a registering photometer of the Moll type in order to obtain curves for publication. Several were photometered to assist in deciphering patterns the measuring of which was not obvious with direct inspection.

Results

The results announced in a preliminary comunication[8] about a year ago, are essentially correct in the light of the complete work. In addition, four anomalous perpendicular components have been found.

In zero field, the probable positions of the five hyperfine structure lines are as follows, reporting as usual the separations from the central "zero" line in milli-angstroms: −25.4, −10.4, 0, +11.5, +21.5. The average deviations from mean are, respectively, 0.3, 0.2, 0 (obviously), 0.2, 0.6. One should mention here an unusual, though I think not significant, fact concerning this last-named line, which explains the large average deviations of the observations of its position. The results of the measurements on the

[6] Schrammen, Ann. d. Physik **83**, 1164 (1927).
[7] McLennan and McLeod, Proc. Roy. Soc. **A90**, 243 (1914).
[8] MacNair, Proc. Nat. Acad. **13**, 430 (1927).

relative positions of the parallel component give +22.1 as the position, while those on the perpendicular components give +21.0. This difference is to be attributed to the fact that the measurement of this line is not easy, at best, and at times is very difficult to obtain with great accuracy, because of the nearness of neighboring lines, as may be seen by inspecting the photometric curves, Fig. 4.

The results of the observations on the behavior of the parallel components are illustrated in Fig. 1, where the relative positions of the lines are plotted against the field strength. Four lines behave normally while the −25.4 line moves toward longer wave-lengths. The solid line drawn through the observed positions of the latter is plotted from the expression Position $= -25.4 + 0.086\ H^{1/2}$ where H is in gausses.

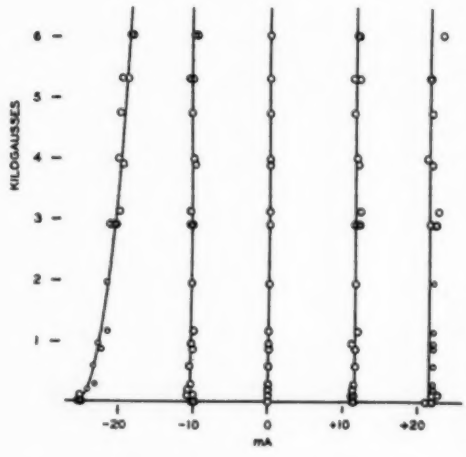

Fig. 1. Parallel components of the Zeeman pattern of the hyperfine structure lines of 2537 of mercury.

The results shown in Fig. 1 indicate that there is no change in the relative positions of the four lines but one questions whether or not there is a shift of wave-length of the whole pattern. Special observations show there is not. This was arrived at by measuring three photographs taken in succession; the first in zero field, the second in a field of 4000 gausses, and the third in zero field again. A shift of the whole pattern toward shorter wave-lengths, for instance, would exhibit itself by a movement of the fringe systems from both sides of the Lummer-Gehrcke plate toward the center of the whole pattern. Now actually the fringe systems of the four lines were in exactly the same place in all three exposures, which gives the answer. The Lummer-Gehrcke plate is not a very appropriate instrument to prove a point of this kind because it is so sensitive to slight temperature changes. For this reason the precaution of taking a third exposure is necessary. The observations of Ellett and myself[3] on the resonance radiation in fields of over 2000 gausses, excited by a resonance lamp (fine line source), also prove that the wave-lengths of these four lines remain constant.

One might draw attention here to the difference in method of obtaining the points plotted as small circles from that of obtaining those plotted as larger circles in Figs. 1, 2, and 3. Where small circles are used it means that two components were so near together that they appeared as one wide fringe. Where these are of about equal intensity one can measure the center of the fringe and from this position and the known position of one of the two components one can infer the position of the other. The assumed position of one and the inferred position of the other are plotted as small circles. Ob-

viously this method gives approximate positions, but it is used only to fill out gaps which would otherwise appear vacant. Also the conclusions of the work would be exactly the same if positions obtained this way were left out altogether. Real bona fide measurements are plotted as larger circles.

The measurements of the *relative* positions of the lines in the short wave-length set of perpendicular Zeeman components are set forth in Fig. 2. No account is taken, for the moment, of the shift of the whole set toward shorter wave-lengths. The dashed lines on the right and left indicate the positions at which the nearest lines of the adjacent orders appear in the Lummer-Gehrcke plate pattern. In view of the behavior of the parallel branch of the -25.4 line, it is to be noted here that its short wave-length perpendicular branch maintains the same relative position throughout the range of field strengths. We shall see, presently, that this is the case also

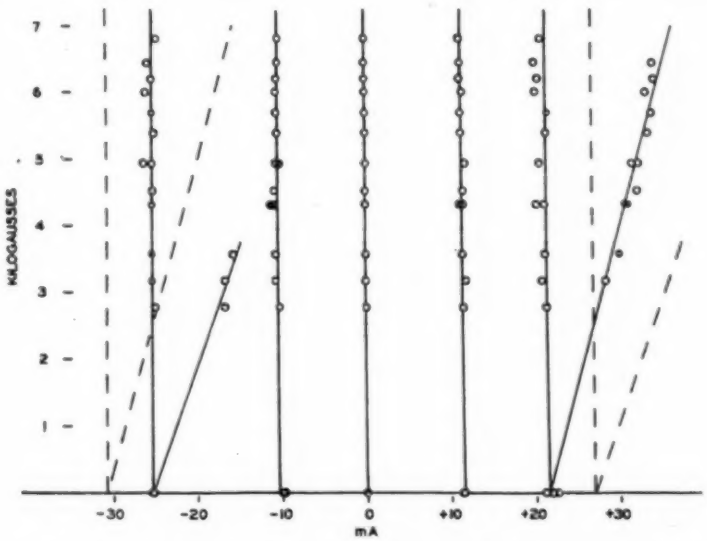

Fig. 2. Relative positions of the short wave-length perpendicular components of the Zeeman pattern of the hyperfine structure lines of 2537 of mercury.

with its long wave-length branch. The striking fact is that two extra components appear. One of these has been attached to -25.4 and the other to $+21.5$, although, because of their low intensity, neither of them can be easily measured in fields below 2700 gausses. The former one, however, can be followed on the plates down to less than 1000 gausses and its existence in a field of 980 gausses is shown by one of the photometric curves in Fig. 4. Above 3800 gausses it apparently fades out altogether. Concerning the second of the extra components, the weakest field in which it appears with certainty is 2760 gausses, which is very near to the point where it crosses the -25.4 line of the next order of the interferometer pattern. Its existence in this field is shown in one of the curves in Fig. 4 by the fact that this fringe is much more dense than that which the -25.4 line alone would make. Below this point, however, one finds no real evidence of its existence. One may say,

then, that this component starts abruptly to move away from the -25.4 line at 2500 gausses, or one may say that it moves on a straight line starting in zero field from $+21.5$ but has very low intensity up to near 2760 gausses above which its existence is certain. The latter seems to be the better choice.

The measurements of the *relative* positions of the lines in the long wave-length perpendicular set of Zeeman components are set forth in Fig. 3, where again, for the purpose of illustration, no account is taken of the shift of the whole set toward longer wave-lengths. This branch of the -25.4 line maintains its relative position throughout. Two extra components are apparent, one attached to -10.4 and the other to $+21.5$. The former is too faint to be measured much below 2000 gausses and is lost again as it approaches -25.4 at 4600 gausses. The second, attached to $+21.5$, cannot be measured below 4000 gausses but can be seen on photometric curves down to 2500. The lower the field, the nearer to $+21.5$ it appears.

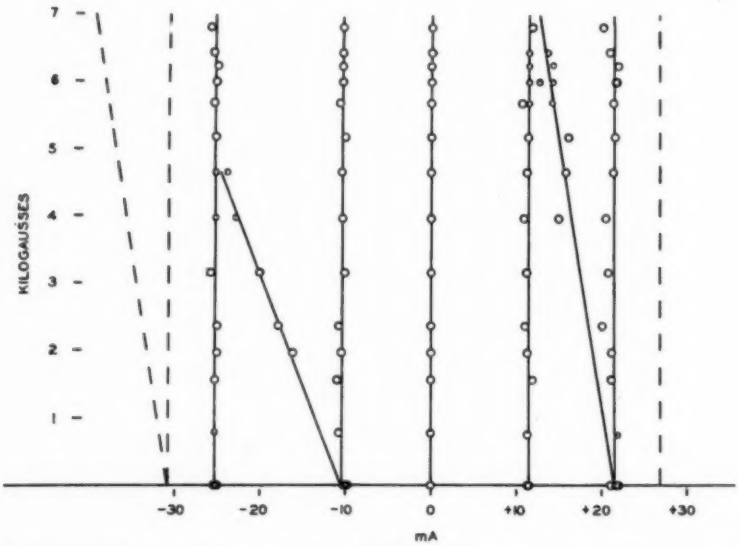

Fig. 3. Relative positions of the long wave-length perpendicular components of the Zeeman pattern of the hyperfine structure lines of 2537 of mercury.

So far we have spoken of the *relative* positions within each set of perpendicular components. To ascertain the actual movement, both sets were photographed together on the same plate by making observations along the magnetic field without a quarter-wave plate in the light path. From the results set forth above we anticipate that there will be far too many components in the pattern to be decipherable. In general this is the case, but there are a few significant exceptions. In a field of 5900 gausses the photograph shows five main fringes disposed exactly like the hyperfine structure lines in zero field. (The two expected faint extra components also appear. See Figs. 2 and 3). Brief consideration shows that this is exactly what one would expect if each line forms two main perpendicular branches having 3/2 the normal Lorentz displacement and is independent of its neighbors

(no Paschen-Back effect). For a line of wave-length of 2537A a 3/2 normal separation means that each perpendicular branch moves away from the

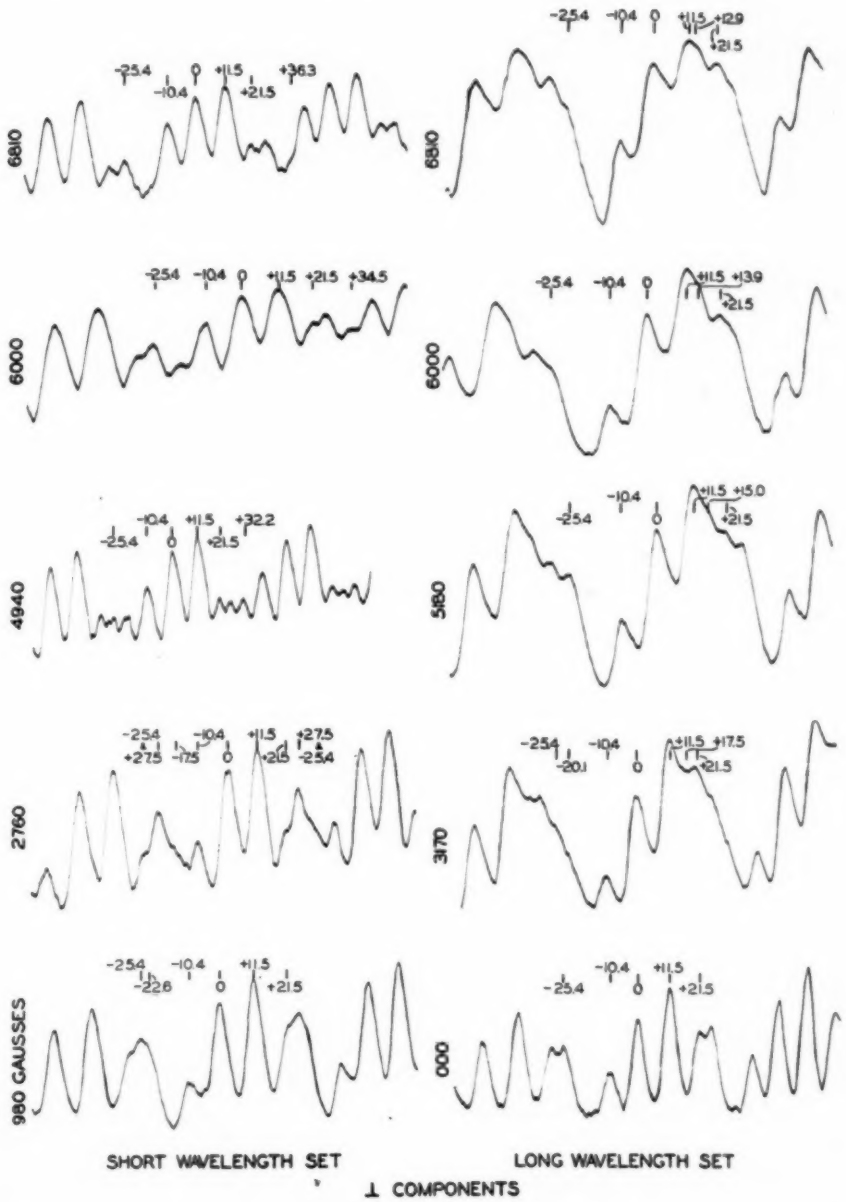

Fig. 4. Photometric curves of Lummer-Gehrcke plate photographs of the perpendicular Zeeman components of the hyperfine structure lines of 2537 of mercury.

zero position at the rate of 4.53 mA per 1000 gausses. In a field of 5780 gausses, then, the two main branches of any one line have moved to posi-

tions which are 26.2 mA on either side of their position in zero field. Since the same thing happens in all orders of the pattern and since the separation of orders for the Lummer-Gehrcke plate used is 52.3 mA (2×26.2) it is apparent that for a field of 5780 gausses the short wave-length components of one order join the long wave-length components of an adjacent order to produce the same pattern one observes in zero field. Since it is difficult to pick out from exposures at various fields, the one at which this coincidence occurs, the difference between 5780 and 5900 is a tolerable error. The conclusion that the main perpendicular components of the hyperfine structure lines have 3/2 the normal separation and show no Paschen-Back effect is supported also by similar observations in lesser field strengths. Now and then a photograph is obtained which can be partially deciphered, especially in fields which superimpose two components. The results in these cases always agree with the above conclusion.

A conventional diagram of the Zeeman effect of λ2537 from zero to 1000 gausses is shown in Fig. 5. The entire width of the figure is less than 0.06A! Assuming that the outside perpendicular components of each line

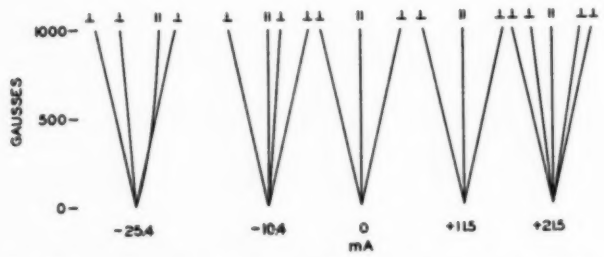

Fig. 5. The Zeeman pattern of the hyperfine structure lines of 2537 of mercury.

have 3/2 the normal displacement, which assumption is substantiated above, we can state the displacements of each of the four extra components. The long wave-length one of +21.5 has 1.08 the normal displacement and the short wave-length one 0.78. The extra component of −10.4 has 0.48 the normal displacement and the extra component of −25.4 has 0.56. In regard to the latter, one should keep in mind the fact that its existence between 0 and 1000 gausses is merely inferred from observations in higher fields (see Fig. 2).

During the past year it has been found that the relative intensities of the hyperfine structure lines of λ2537 of mercury vary with the operating conditions of the arc regardless of any change a magnetic field causes. Miss Schrammen[6] has also observed this phenomenon. Until the reason for this behavior is cleared up one doubts the importance of measuring the relative intensities in various fields. The unusual changes in the relative intensities reported in the preliminary communication of this work may be the direct result of the magnetic field or may be only an indirect result, due to the increased current density, for instance. It seems that little more can be said in this regard at present.

Discussion of Results

In the first place we attempt to answer a possible criticism of the use of a helium-mercury discharge. Let us consider, for a moment, the observations of the parallel Zeeman components illustrated in Fig. 1. No distinction has been made between the results from four different sources, namely, He-Hg arc number 1 (He pressure 21 mm), He-Hg arc number 6 (He pressure 30 mm), an ordinary vacuum mercury arc, and a submerged water-cooled vacuum mercury arc. One set of points plotted for zero field is from He-Hg arc number 1 and the other two sets from He-Hg arc number 6. The points for 100 gausses are from the ordinary vacuum mercury arc mounted so that the field pressed the discharge against the side of the tube toward the spectrograph. Most of the other points up to 1200 gausses are from the submerged water-cooled arc. The points for 965 gausses are from He-Hg arc number 1 as are about half of all the others. The remainder are from He-Hg arc number 6. Certain it is, then, that the peculiar movement of the parallel branch of -25.4 is the same whether one uses a vacuum arc source or a He-Hg arc source and in the latter case it is immaterial whether the helium pressure is 21 mm or 30 mm. The study of the perpendicular components was carried out with arcs all having about the same helium pressure, namely, 28 mm.

Wood has studied the hyperfine structure of $\lambda 2537$.[4] The separations of the five lines which he reports may be expressed in milli-angstroms as follows: -24, -10, 0, $+11$, $+22$. The results of the present work (see Fig. 5) check these observations very nicely, especially so when one realizes that with the disposition of apparatus used by Wood one really observes the parallel Zeeman components in a field of 100 gausses, or somewhat more. (The field was used to press the discharge against the wall of the arc to prevent reversal.) In this field strength our -25.4 line has moved to about -24. Miss Schrammen[6] also reports the structure of this line as: -24.3, -10.2, 0, $+11.1$, $+21.5$. The Lummer-Gehrcke plate she used was of such thickness that the -24.3 line of one order practically coincided with the $+21.5$ line of the next. There is good agreement between her measurements of the other three lines and those presented here.

Wood[4] has studied somewhat the Zeeman effect of the hyperfine structure lines of $\lambda 2537$. In one case he was able to split the interference dots into distinct components. He also made some observations on the effect of a magnetic field on the absorption of mercury vapor. At first sight the present work appears to contradict his results. One cannot subscribe to this view, however, without a knowledge of the exact value of the field strength and its uniformity throughout the absorption cell. This latter is important as it determines in a large measure the effective width of the absorption lines.

The results of Ellet and myself[3] on the polarization of the hyperfine structure lines of $\lambda 2537$ in resonance radiation, excited by polarized light, must be initimately connected with the Zeeman effect of these five lines. The

three middle lines we found to be 100 percent polarized and the two outside lines incompletely polarized. Referring to Fig. 5, one sees that of the five lines these two have the most peculiar Zeeman patterns. Two of the other three give 3/2 normal triplets but the third (−10.4) has one extra component. One must say, then, that the appearance of this extra component does not cause the −10.4 line to be incompletely polarized in resonance radiation. It seems, however, that these two researches, taken together, certainly warn one not to make definite theoretical deductions from the many experiments on the resonance radiation of mercury until more is known of the origin of the hyperfine structure of the energy levels of this element. One would feel much safer, in this regard, in dealing theoretically with results of resonance radiation experiments on elements the lines of which show no structure. Several of the lighter elements are known to satisfy this requirement and probably many of them do.

In closing, I wish to express my appreciation to the authorities of the Naval Research Laboratory for the use of one Lummer-Gehrcke plate and the registering photometer, and to the members of the heat and light division of the same laboratory for the hospitality extended to me.

BUREAU OF STANDARDS,
WASHINGTON, D. C.,
February 15, 1928.

THEORY OF THE EXCITATION OF SPECTRA BY ATOMIC HYDROGEN

By Joseph Kaplan*

Abstract

An explanation is proposed for the results of Bonhoeffer and of Mohler on the excitation of spectra by atomic hydrogen. The theories advanced by these authors do not completely explain the experimental results. The theory presented here is based on the hypothesis that in a three-body collision two hydrogen atoms can be bound to form a molecule in any one of the vibration states of its normal electronic level. We make use of the principle, used in collisions of the second kind, that the probability of excitation increases as the energy of the exciting body and the energy necessary for excitation approach each other. This is done by postulating that the probability of the excitation of the third body is greater, the nearer the energy required is to the difference between the energy of recombination and the energy retained by the hydrogen molecule in one of its vibration states. The theory has been applied successfully to the excitation of Na, K, Cd, Zn, Cs and Mg by atomic hydrogen. The excitation of the 2537 line of mercury, which requires more energy than that available from recombination, is explained on the basis of Bonhoeffer's observations.

BONHOEFFER[1] and later Mohler[2] found that spectra could be excited when certain vapors are allowed to mix with atomic hydrogen. Spectra are also excited at surfaces by atomic hydrogen; the cases treated here will however, with one exception, be ones in which the spectra are excited in the vapor. It is well known now that the long life[3] of atomic hydrogen under certain conditions is due to the fact that two atoms of hydrogen do not combine to form a molecule unless a third body is present. The role of the third body is to make it possible to satisfy the laws of conservation of energy and momentum during the process of binding. The most obvious explanation therefore of the excitation of spectra in the vapor phase by atomic hydrogen is that the atom or molecule that is excited acts as a third body when two atoms of hydrogen combine to form a molecule. The energy of excitation of the third body will come from the energy liberated when the recombination takes place.

A marked peculiarity however of the experimental results of both Bonhoeffer and Mohler is that very often a line is not excited even though the energy available in a three-body collision is enough to excite the line. As an example, one can cite the case of sodium for which the 3^2P states require about 3.7 volts and the 2^2P state 2.08 volts. It is found that the 2^2P state is strongly excited and that the 3^2P state is unexcited. Similar cases occur for zinc, magnesium and other metallic vapors. It is apparent therefore that the simple explanation suggested above is not correct.

* National Research Fellow in Physics.

[1] Bonhoeffer, Zeits. f. Phys. Chem. **116**, 391 (1925).

[2] Mohler, Phys. Rev. **29**, 419 (1927).

[3] Kaplan, Phys. Rev. **30**, 639 (1927).

Another explanation proposed by Mohler was that first a metal hydride XH and hydrogen atom forms H_2 and an excited atom X′, having energy $Q_{X'}$. The reaction is

$$H+XH \rightarrow H_2+X'+Q_{H_2}-Q_{XH}-Q_{X'}$$

where Q_{H_2} is the heat of dissociation of hydrogen, 4.34 volts. This reaction will take place if $Q_{X'} \leqq Q_{H_2}-Q_{XH}$. The above explanation will obviously account for the absence of some lines belonging to an element and the presence of others. Mohler does not apply the theory to test individual cases, probably because the heats of formation of most of the metallic hydrides are not known. In this theory one should expect that if any lines of an element are excited they must be the lines of lowest excitation potentials and a glance at Table II will show this to be true. Mohler suggests that the hydride is formed at a liquid or solid surface and eliminates therefore the possibility of excitation when only the vapor is present.

Applying Mohler's theory to the case of sodium one finds that the test $Q_{X'} \leqq Q_{H_2}-Q_{XH}$ predicts the excitation of the 3.6 volt $3D$ states. Here $Q_{XH}=0.72$ volts so that $Q_{X'}$ must be less than $4.34-0.72=3.62$ volts. It is seen however that the $3D$ level is not excited so that the theory fails in this particular case. Since the heats of formation of the hydrides are not known for the other elements in the table it is not possible to test this theory further.

Bonhoeffer, Mohler and the author have observed that the 2537 line of mercury was excited when the surface of liquid mercury was bombarded by atomic hydrogen. Bonhoeffer observed in addition that the 2537 line was not excited when only the vapor was present, but that the presence of excited mercury hydride was necessary. The 2537 line was only weakly excited whereas the mercury hydride bands were strongly excited. Since the energy necessary to put the mercury atom into the 2^3P_1 state, from which 2537 is radiated, is 4.86 volts, it is apparent that neither the three-body theory nor the hydride theory of Mohler will account for the excitation of 2537. In the following a new explanation is proposed for the excitation of spectra by atomic hydrogen and for the excitation of 2537.

TABLE I. *Values of E_n and R_n.*

Vibration Number	E_n	$D-E_n$	Vibration Number	E_n	$D-E_n$
0	0	4.34	6	2.66	1.68
1	.51	3.83	7	2.99	1.35
2	1.00	3.34	8	3.30	1.04
3	1.47	2.89	9	3.59	.75
4	1.88	2.46	10	3.84	.50
5	2.28	2.06	11	4.05	.29

In what follows D will represent the heat of dissociation of hydrogen. E_n will represent the energy possessed by the hydrogen molecule in the nth vibration states of its normal electronic level and R_n will be used to represent

the difference $D-E_n$. In Table I the various values of E_n and R_n calculated from the absorption spectrum results of Dieke and Hopfield,[4] are tabulated.

In all the discussions of the formation of H_2 from atoms it has been assumed that when two atoms of hydrogen meet in the presence of a third body, the resulting product is a normal hydrogen molecule with zero vibrational quantum number. This makes it necessary that all of the energy of recombination be transferred to the third body. Until now no discussion as to a controlled transfer of the energy of recombination has been given. The theory presented in this paper discusses in more detail than has heretofore been done, the transfer of the energy of recombination to the third body.

The normal hydrogen molecule is known to have vibrational states, from which it cannot radiate; the only way of returning to its stable non-vibrating state being by the loss of its vibrational energy by a collision. Now in the excitation of spectra by collisions of the second kind the probability that a collision be an inelastic one increases as the energy of the exciting particle gets closer to that required for the excitation. This principle prompts the idea that in cases where one of the R_n's given in Table I is equal to or very nearly equal to the value of an excitation potential of the vapor mixed with the atomic hydrogen, then it will be highly probable that the particular level will be excited in a three-body collision. A process of this kind implies that the two hydrogen atoms are only partially bound during the collision, R_n being the part of the energy of recombination that is transferred to the third body and E_n the remaining part, which is retained by the molecule as vibrational energy. E_n it will be remembered is the energy possessed by the molecule in its nth vibrational state. The above theory states therefore that two hydrogen atoms can be bound into molecules in the various vibrational states, a particular state being favored if the third body has an excitation potential corresponding to the difference between the energy of recombination and the energy retained by the molecules as vibrational energy. This statement must of course be slightly modified when the changes in kinetic energy during a three-body collision are considered. These changes will however be very small under the conditions of the experiments, and will be neglected in the present discussion. Some of the data of Table II are taken from Mohler's paper and will be discussed from the point of view of the theory. The 5890–5896 lines of sodium are strongly excited. They require 2.09 volts and R_5 is equal to 2.06 volts. The D lines of sodium are probably the most strongly excited lines of any vapor so far tried and the agreement with the theory is seen to be good. The sodium lines that originate on the $3D$ levels are absent. These lines require 3.6 volts whereas the nearest R's are R_1 and R_2 having values of 3.83 and 3.34 volts respectively. Similarly the lines originating on the $3P$ levels and requiring about 3.7 volts are also absent.

The lines of potassium at 7665–7699A and originating on the $2P$ levels were very faintly excited in a twelve hour exposure on stained plates.

[4] Dieke and Hopfield, Zeits. f. Physik **40**, 299 (1926).

TABLE II. *Lines excited by atomic hydrogen.*

Element	λ	Excitat. Pot.	Intensity	Nearest R	Difference
Na	5890	2.09	strong	$R_5=2.06$	0.03
	8183	3.6	absent	$R_1=3.83$	0.23
	3302	3.7	absent	$R_1=3.83$	0.13
K	7655	1.61	weak	$R_6=1.68$	0.07
	4044	3.0	absent	$R_3=2.87$	0.13
Cs	All Lines	1.38 to 3.87	absent	$R_7=1.35$	0.03
				$R_1=3.83$	0.04
Mg	4571	2.70	absent	$R_3=2.87$	0.17
Cd	3261	3.78	strong	$R_1=3.83$	0.05
Zn	3076	4.01	absent	$R_1=3.83$	0.18
Hg	2537	4.86	weak		
HgH	4520 to	3.1 to			
	3274	3.8	strong		
Tl	5350	3.26	absent	$R_2=3.34$	0.08

The excitation potentials of the $2P$ levels are about 1.60 volts and the nearest R_n is $R_6=1.69$ volts. This fact indicates that as in the case of collisions of the second kind, the excitation is stronger the nearer the available energy is to the required energy. This is seen to be the case when sodium and potassium are contrasted. The lines originating on the $3P$ levels are absent. The excitation of these levels requires about 3.0 volts and the nearest R_n is 2.87 volts. It may be noticed that the nearest R_n in this case is less than the required energy. It may be that when the nearest R_n is less than the required energy the process is less probable than when it is greater even though the difference be the same in both cases.

All the lines of caesium are missing. A line of caesium that should be excited is the resonance line at 8943A requiring 1.38 volts. The nearest R_n is R_7 equal to 1.35 volts. Its absence on the photographic plate is not surprising since photography at such a wave-length is difficult. The caesium was at 200° and the exposure was four hours. Although higher levels corresponding to R_1 should be excited, further experiments are necessary before one can definitely say whether or not they are present. Both Bonhoeffer and Mohler observed a transient surface fluorescence showing a continuous spectrum similar to the spectrum of caesium in the Bunsen flame.

Magnesium, heated to 600°C, showed no lines. The resonance lines of magnesium require 2.7 volts and 4.34 volts respectively and although the 2.7 line should not appear on this theory the 4.34 volt line should be excited. The 4.34 volt resonance line of magnesium may have been absent for the same reason as the line of thallium at 5350A. This line requires 3.27 volts and the nearest R_n is R_2, equal to 3.34 volts. In the case of thallium the metal was heated to 600° and the vapor pressure of thallium at 600° is only one-fifth of the vapor pressure of cadmium at 350°. Now cadmium at 350° is strongly excited by atomic hydrogen, the required energy being 3.78 volts and the nearest R_n being R_1, equal to 3.83 volts. It seems that in order to get excitation even in favorable cases the vapor pressure must be about equal to that of cadmium at 350°, so that the cases of both thallium and magnesium bear repetition.

The zinc resonance line at 3076A was not excited. The author, in repeating some of these experiments, exposed a plate for twenty-four hours and was unable to observe this line. The energy necessary for its excitation is 4.0 volts and the nearest R_n is R_1 equal to 3.83 volts so that its absence is to be expected.

We return now to the excitation of the 2537 line of mercury which cannot be explained on any of the three theories mentioned. Bonhoeffer found that when liquid mercury was bombarded by atomic hydrogen a blue flame developed above the surface of the liquid mercury. The heating at the surface due to the recombination of hydrogen atoms is sufficient to cause considerable evaporation of mercury vapor. The same phenomenon was observed by the author when solid cadmium was bombarded by atoms of hydrogen. The evaporation of cadmium was sufficient to give the 3261 line after about a four hour exposure. A film of cadmium was deposited on neighboring parts of the tube. It is quite certain therefore that considerable Hg vapor must be formed at the surface of mercury.

The blue glow above the mercury surface possesses some rather interesting characteristics. It shows the spectrum of mercury hydride rather strongly developed and after a ten hour exposure gave the 2537 line only feebly. When the blue flame is photographed in a camera with quartz lenses the shape of the flame on the picture is the same whether it is photographed in the total radiation from the flame or only in the radiation of wave length 2537. This fact was shown by Bonhoeffer and indicates that the 2537 line is excited only in the presence of excited mercury hydride molecules. Bonhoeffer also showed that when the evaporation of mercury was very rapid the blue flame disappeared because the atomic hydrogen was unable to diffuse against the rapid opposing stream of mercury vapor. Neither Bonhoeffer nor the author have been able to excite 2537 when only the vapor is present i.e., under conditions similar to the cases of Cd, Na, etc. The important experimental fact that the Hg line 2537 is excited only when liquid mercury is bombarded by atomic hydrogen and furthermore only in the presence of excited hydride molecules must be considered in any explanation of the presence of 2537. The explanation of the excitation of the 2537 line of mercury which is proposed by the author is the following. A collision between an excited hydride molecule and a single hydrogen atom results in the formation of a normal hydrogen molecule and an exicted mercury atom in the 2^3P_1 state. The reaction is as follows

$$\mathrm{Hg\,H(exc.)+H\rightarrow Hg(exc.)+H_2}$$

The energy available for the excitation of the Hg atom in such a process is the difference between the energy of excitation of the hydride molecule plus the energy of recombination of the hydrogen molecule and the energy of dissociation of the hydride molecule. The latter energy is equal to 0.37 volts, according to the band spectrum data of Hulthén.[5] The energy of excitation

[5] Hulthèn, Zeits. f. Physik **32**, 32 (1925).

of the hydride molecule varies from 3.1 to 3.8 volts for the bands observed in the blue flame. The energy available for excitation varies therefore from $(4.34+3.1-.37)$ to $(4.34+3.8-.37)$ i.e., from 7.07 volts to 7.77 volts. These amounts of energy are more than sufficient to excite the 2537 line of mercury and the 1849 line as well. The latter may have been present but its observance under the conditions of the experiments would have been impossible because of the intense absorption of the 1849 line by mercury vapor. We may cite two arguments in support of this explanation. First, the weak excitation of the 2537 line as compared to the hydride bands indicates that the process is secondary. Secondly, the experiments of Bonhoeffer show conclusively that the 2537 line is observed only in the part of the tube where the hydride bands are also observed, indicating that the presence of excited hydride molecules is essential for the excitation of the 2537 line.

Further experiments on the excitation of spectra by atomic hydrogen will be carried out with the hope that eventually more data will be available to test the theory of three-body collisions proposed here. The writer wishes to thank Professor K. T. Compton for the privilege of carrying on this work at the Palmer Physical Laboratory.

PRINCETON UNIVERSITY,
March 3, 1928.

A THEORY OF THE ELECTRIC DISCHARGE THROUGH GASES

By Philip M. Morse

Abstract

Three general differential equations are set up which determine the average behavior of a discharge of electricity through a gas. Approximate solutions, giving the electric field E and the concentration of electrons and positive ions, n_1 and n_2, at any distance x from the cathode, are found for several ranges of value of E.

When E is large, the solution corresponds to the conditions in the *cathode* and *anode fall spaces* in a glow discharge. Equations are obtained for the potential drop V across the fall space; the current density at the electrode divided by the square of the gas pressure, j/p^2; and the thickness of the fall space times the pressure, pd.

These equations indicate that for the cathode fall space there is a certain minimum value of V, called V_n; and for j/p^2, called j_n/p^2; and a corresponding maximum value of pd, pd_n, beyond which values the discharge ceases. These stationary values are shown to be constants, dependent only on the nature of the gas used and of the cathode material, and correspond to the *normal cathode fall space*. The equation determining V_n is shown to be of the right form by comparison with the experimentally determined values. From these values of V_n, values of j_n/p^2 and of pd_n are calculated for four gases and four cathode materials, and the calculated values check with the experimental data. The corresponding equations for the *anode fall space* show why there is no corresponding normal anode fall.

A consideration of the discharge when E is large throughout the distance between electrodes indicates that there is another stationary value of the cathode fall space when the current density at the cathode reaches its maximum possible value. The V in this case is much smaller than the V_n for the glow discharge, and the form of the equations indicate that they describe the conditions in an *electric arc*.

Another approximate equation is obtained when E is constant, which is the case in the *positive column* of a glow discharge. This solution indicates that within certain limits of pressure and current density, small sinusoidal variations about the average value E_p, are possible in E. These correspond to the *striations* sometimes observed in the positive column. The equations determining E_p and those determining the distance between striations check with the known empirical laws relating these amounts to the pressure, the radius of the discharge tube and the critical potentials of the gas used. A general discussion is given of the *Faraday dark space* and reasons are given why it should be near the cathode rather than the anode.

WHEN electricity passes through a gas from one plane electrode to another parallel to it, the phenomena taking place are many and complicated. A certain number of positive ions falling on the cathode per second will, by some undetermined mechanism set free an electron which will travel to the anode, ionizing and exciting the gas molecules in its path. In order to maintain the discharge in a steady state, this electron must set free just enough ions in a second to cause another electron to be ejected from the cathode; or else, if any excess over this requisite number is created, this excess must disappear by recombination before striking the cathode.

It seems probable that this ratio between the number of positive ions striking the cathode per second and the number of electrons ejected per

second (i.e., the ratio between the positive ion current to the cathode and the electron current from it) is dependent on the nature of the gas in the tube, on the material of the cathode, and on the velocity of the positive ions striking the cathode. This, of course is not true if the cathode is emitting photo- or thermo-electrons independent of any positive ion bombardment, as in the electric arc or with a heated cathode.

At any point in the body of the discharge, ions are being produced by electron impact, are disappearing by recombination, are diffusing away, and are being carried away by the electric field. This whole set of reactions is limited by Poisson's relation between the concentration of ions and the variation of the electric field.

The complete solution of this phenomenon is, of course, impossible, primarily because the gas is a discontinuous material, and we have no means of determining the exact velocity of any ion at any place under any field. However, average values for this velocity have been developed which have considerable accuracy, and likewise statistical relations between the average number of ions caused by an electron and the electric field are known.

If we assume that these relations for mobility and for ionization account for all these actual random motions, we can consider that the gas is a continuous fluid, and that each ion has a definite terminal velocity at any point in the tube, and the problem becomes much simpler. This statistical method of solution is probably quite accurate, if the smallest lengths considered are of a larger order than the length of a mean free path, and if the concentration of ions be fairly large. The shortest distance we shall find necessary to consider is of the order of 50 to 100 mean free path lengths, and the smallest concentration of ions is about 10^7, so the statistical method is quite justifiable.

If n_1 and n_2 are the concentration of electrons and positive ions at any point distant x from the cathode, v_1 and v_2 their respective average drift velocities, and E is the field strength at that point, then the following relations can be set up for a stable discharge in a tube of unit cross section:

$$dE/dx = 4\pi e(n_1 - n_2) \tag{1}$$

$$n_1 v_1 \alpha - R + D_1 d^2 n_1/dx^2 - d(n_1 v_1)/dx = 0 \tag{2}$$

$$n_1 v_1 \alpha - R + D_2 d^2 n_2/dx^2 - d(n_2 v_2)/dx = 0 \tag{3}$$

The first equation is that of Poisson with the sign changed since we are reckoning the direction from cathode to anode as positive. The last two equations represent the fact that for equilibrium, the number of ions formed per second per cc, the number disappearing by recombination, the number diffusing away, and the number being pulled away by the electric field, must add up to zero.

The term α in Eqs. (2) and (3) is the number of ions formed per cm path by an electron travelling under a field E, and with a corresponding velocity v_1. A quite accurate relation between α and E has been developed by Townsend,[1] and is that

[1] Townsend, "Electricity in Gases," Chapter VIII.

$$\alpha = pN\epsilon^{-pNv_0/E} = pNz \tag{4}$$

D_1 and D_2 are the diffusion constants for positive and negative ions, and are proportional to their mobilities, μ_1 and μ_2 of the respective ions[2] according to

$$D_1 = D\mu_1 \; ; \; D_2 = D\mu_2 \tag{5}$$

At low field strengths $D = kT/e$, but for high fields, D is probably dependent on the gas in the tube.

R is the number of ions which recombine or disappear in some way from the discharge per cc. There are a certain number recombining by collision, but it has been shown[3] that the greater number of recombinations take place at the walls of the tube. However as R is small it need only be considered when dealing with the positive column or the Faraday dark space, so its discussion will be postponed until then.

The velocities will equal the mobilities times the field strength. Inasmuch as E will in most cases be large, the most accurate value[4] for these mobilities will be

$$\mu_2 = 0.815\left(\frac{e\lambda_2}{Ep(M^2/1.134)^{1/2}}\right)^{1/2} = \frac{u}{(Ep)^{1/2}}$$

$$\mu_1 = 0.815\left(\frac{e\lambda_1}{Ep(Mm/1.134)^{1/2}}\right)^{1/2} = \frac{au}{(Ep)^{1/2}} . \tag{6}$$

In the case of the Faraday dark space, however, as we shall see later, E is very small. In this case, the most accurate values of the mobilities will be

$$\mu_2' = 0.815\frac{e\lambda^1}{(2MKT)^{1/2}} = \frac{u'}{p} \; ; \quad \mu_1' = a'u'/p \tag{7}$$

λ_1 and λ_2 are the mean free paths of the electron and of the positive ion at 0°C and 1 mm pressure, and p is the pressure in mm of mercury. The terms a and u are dependent only on the gas used; u is the constant factor in the mobility of the electron, which is fairly accurately known; a is the ratio between the mobility of the electron and of the positive ion. It is not necessary to know this accurately, since we shall see later that if it is large enough that $a+1$ or $a-1$ are practically equal to a, this factor cancels out.

Making these substitutions, Eqs. (2) and (3) become

$$aNpzn_1E^{1/2} - Rp^{1/2} + \frac{aD}{E^{1/2}}\frac{d^2n_1}{dx^2} - a\frac{d(n_1E^{1/2})}{dx} = 0 \tag{8}$$

$$aNpzn_1E^{1/2} - Rp^{1/2} + \frac{D}{E^{1/2}}\frac{d^2n_2}{dx^2} + \frac{d(n_2E^{1/2})}{dx} = 0 \tag{9}$$

[2] J. J. Thompson, Conduction of Electricity Through Gases, Second Edition, pp. 42 and 43.
[3] W. Schottky, Phys. Zeits. **25**, pp. 635 (1924).
[4] K. T. Compton, Phys. Rev. **22**, 333 (1923).

The two, with Eq. (1), will completely determine n_1, n_2 and E for any x and for any boundary conditions.

A complete solution of these equations is impracticable. However, the three most interesting parts of the glow discharge (the cathode and anode falls, the Faraday dark space, and the positive column), and the whole of such discharges as the electric arc, are really special cases of the general solution. In the fall spaces in the glow discharge and in the arc, E is quite large; in the Faraday dark space E is very small; and in the positive column E, n_1 and n_2 are comparatively constant.

CASE I. When E is large Eq. (8) becomes $d(n_1E^{1/2})/dx=Npzn_1E^{1/2}$, or $n_1E^{1/2}=-c\epsilon^{pN\int zdx}=-c\epsilon^{pNx}$, since z is practically unity for large values of E. From Eq. (9) $n_2E^{1/2}=ac\epsilon^{pNx}$. From these two equations and from Eq. (1)

$$E=c'\epsilon^{2pNx/3}+c_0 \tag{10}$$

This would be the form of the field distribution at the anode. By turning the tube around, solving, and then returning to our original coordinates, with $x=0$ at the cathode, after solving we obtain,

$$E=c''\epsilon^{-2pNx/3}+c_0' \tag{11}$$

as the form of the field distribution near the cathode. This same form of distribution has been obtained by other methods by Compton and Morse.[5] They obtained as the exponential factor $kpNx$, where k was about 0.6. The two methods thus check each other.

THE CATHODE FALL

Observations have shown that the greatest fall in potential across the discharge occurs close to the cathode. At the end of this fall the electric field comes to its minimum value, and the gas becomes luminous. Up to certain currents this space assumes an equilibrium state; i e., the potential drop across the space is a constant independent of the pressure, its thickness is inversely proportional to the pressure, and the current density at the cathode is proportional to the square of the pressure, the current concentrating on a patch of this density. This state is called the *normal cathode fall.*

As the total potential across the tube is increased, the patch of cathode receiving current increases, but otherwise conditions across the fall remain the same, until the patch has covered the whole cathode. A further increase in applied potential increases the current density, increases the drop in potential across the space, and decreases its thickness slightly. This state is called the *abnormal cathode fall.*

If V_n is the normal fall in potential across the space, V_a the abnormal, j_n and j_a the normal and abnormal current densities, and d_n and d_a the respective thicknesses of the space, then:

[5] K. T. Compton and P. M. Morse, Phys. Rev. **30**, 305 (1927).

$$V_n = \text{constant} \; ; \; V_a > V_n \tag{12}$$

$$j_n/p^2 = \text{constant} \; ; \; j_a > j_n \tag{13}$$

$$pd_n = \text{constant} \; ; \; d_a < d_n \tag{14}$$

where these constants are determined by the gas and the cathode material. These empirical relations will serve to check the solution.

If we assume values for n_1, n_2 and E from Eq. (11), and substitute these in some modification of Eqs. (8) and (9), values of the constants c should be obtained which will hold approximately throughout the cathode fall. Assume that $n_1 = A - (A - n_1^0)\epsilon^{-2pNx/3}$, $n_2 = A + a(A - n_1^0)\epsilon^{-2pNx/3}$ where n_1^0 is the electron density just outside the cathode. From Poisson's equation [Eq. (1)], and from these two

$$\frac{dE}{dx} = -4\pi e(a+1)(A - n_1^0)\epsilon^{-2pNx/3}$$

Thus our assumption fits the requirements of Eq. (11), and also fits the conditions required at the cathode. Substituting these in the equation formed by subtracting Eq. (9) from Eq. (8), it is found that

$$A = \frac{4}{9\pi}\frac{Dp^2N^2}{e(a+1)} \tag{15}$$

Therefore if we can determine the value of D, N and a and n_1^0 the ion concentrations and field can be determined at any point in the cathode fall. The electron concentration at the cathode n_1^0, is naturally of the same dimensions as A, so we can let it equal Ac where c is some constant representing the electron emission of the cathode, and probably dependent only on the cathode material. Then the three equations become:

$$n_1 = A\left[1 - (1-c)\epsilon^{-2pNx/3}\right] \tag{16}$$

$$n_2 = A\left[1 + a(1-c)\epsilon^{-2pNx/3}\right] \tag{17}$$

$$E = (8/3)DpN(1-c)\left[\epsilon^{-2pNx/3} + E_a\right] \tag{18}$$

where E_a is a constant of integration to be determined later.

The current density of electrons from the cathode will be $e\mu_1 E n_1$, evaluated at the cathode.

$$j_a^- = \frac{4}{9\pi}\left(\frac{8}{3}\right)^{1/2} D^{3/2}N^{5/2}up^2c(1-c)^{1/2}(1+E_a)^{1/2} = Bp^2c(1-c)^{1/2}(1+E_a)^{1/2} \tag{19}$$

where B depends only on the nature of the gas. Similarly:

$$j_a^+ = Bp^2(1-c)^{3/2}(1+E_a)^{1/2} \tag{20}$$

The ratio between j_a^+ and j_a^- is the number of positive ions required to strike the cathode for each electron emitted. This probably is a constant dependent on the cathode material and on the velocity of the positive ions striking the cathode. This velocity is

$$u[8DN(1-c)/3]^{1/2}(1+E_a)^{1/2}$$

a constant independent of the pressure and dependent on E_a and the gas and cathode material. The ratio, from Eqs. (19) and (20), is $(1-c)/c$. The reciprocal of this, which is the "fraction" of an electron ejected for each positive ion striking the cathode, is therefore independent of the pressure, and will probably increase as the positive ion velocity increases. That is,

$$c/(1-c)=2H(1-c)^{1/2}(1+E_a)^{1/2}/9 \text{ or } 1-c=1-H(1+E_a)^{1/2} \tag{21}$$

where H is very small. This relation is not accurately true, but in any case $1-c$ will decrease slightly as E_a increases.

The total current to the cathode is

$$j_a=Bp^2(1-c)^{1/2}(1+E_a)^{1/2} \tag{22}$$

which corresponds to the requirements of the first part of Eq. (14).

So far we have been dealing with conditions near the cathode, where E is large, and z is practically unity. If we wish to investigate the conditions near the end of the cathode fall, just before the equations of Case I break down, we must consider z more carefully. Taking the value of z from Eq. (4), expanding, and then integrating, it is found that, approximately

$$\int z\,dx = x-Ge^{2pNx/3} \quad \text{where} \quad G=v_0/32D(1-c)$$

which is very small, as we shall see later. Therefore our approximation that $\int z dx$ equals x is legitimate as long as the quantity which contains it is large throughout the fall space. This means that Eqs. (16) and (17) hold fairly well to the end of the fall space. However, E becomes small at the end, so we must include this second term to determine just where E becomes zero, if it does. E becomes

$$E=\frac{8}{3}Dp\,N(1-c)\left[e^{-2pNx/3}-\frac{pNv_0x}{48D(1-c)}+E_a\right] \tag{23}$$

The integral of E, the potential V, is large at the end of the space, and so this second term can be omitted, giving

$$V=4D(1-c)-4D(1-c)e^{-2pNx/3}+8DN(1-c)E_apx/3 \tag{24}$$

It is rather difficult to determine exactly where these equations break down entirely, that is, where the cathode fall ends. A reasonable assumption would be that it ends (i.e., $x=d$) when $E=8DpN(1-c)E_a/3$.

A more probable assumption would be to find the number of positive ions formed per second through a distance x from the cathode, and set x equal to d when this integral equals j_a^+. That is we consider the positive ion current to the cathode as being entirely due to those positive ions formed within the fall space, and that those formed outside, a much smaller number, are lost through recombination. This seems plausible, inasmuch as E becomes

very small at the end of the fall space, so small that very few of the ions formed in the positive column can get across to the cathode.

However, when the integration is carried out, and the integral set equal to j_a^+, we find that when $x=d$, E must equal $8DpN(1-c)E_a/3$. So the original assumption was correct.

But when this is so

$$\epsilon^{2pNd_a/3}=v_0pNd_a/48D(1-c) \quad \text{or} \quad Npd_a=\frac{3}{2}\log\left[\frac{48D(1-c)}{v_0Npd_a}\right] \tag{25}$$

This shows that pd_a is a constant, and therefore, by Eq. (24), V at d, *i.e.*, V_a, must be a constant, and therefore the first parts of the empirical equations (12) and (14) are satisfied.

Thus for a given pressure, gas, cathode, and E_a, the three measurable quantities j_a/p^2, pd_a and V_a are definite and determinable. The only constant which is not determined by these physical conditions, but which can be given any value, is E_a. Let us see what happens when it is increased. By Eq. (21) $c/(1-c)$ increases, or $1-c$ decreases slightly. By Eq. (22) j_a increases, by Eq. (24) V_a increases, and by Eqs. (21) and (25), pd_a decreases slightly.

Thus any change in either of the three quantities, say in j_a, produces a definite change in the other two. This must correspond to the conditions of the abnormal fall. Let us see if we can obtain a condition similar to the normal cathode fall.

The Normal Cathode Fall.

As E_a is allowed to vary, we see that its minimum allowable value is zero. For if E_a were a minus quantity, the number of ions formed per second within the fall space will be less than j_a and the discharge will cease.

Then j_a has a definite minimum value

$$j_n=Bp^2(1-c)^{1/2} \tag{26}$$

and V_a has a definite minimum value, given approximately by

$$V_n=4D(1-c) \tag{27}$$

and pd_a has a definite maximum value given by Eq. (25) when $(1-c)$ has its maximum value.

These stationary values are obviously those of the normal cathode drop. If all the constants, N, v_0, D, u and c were known for any particular cathode and gas, it would be possible to calculate V_n, pd_n and j_n/p^2 from them directly. However, the values of D and c are not known.

But since we have shown that V_n is a constant, though its value cannot be calculated with the data available, and since both D and c occur in the expression for V_n, we can use the experimentally determined values of V_n to determine the related values of pd_n and j_n/p^2. Thus

$$pd_n=\frac{3}{2N}\log\left(\frac{12}{N}\frac{V_n}{pd_nv_0}\right) \tag{28}$$

and, approximately:

$$\frac{j_n}{p^2}=\frac{4}{9\pi}\left(\frac{8}{3}\right)^{1/2} N^{5/2}u\left(\frac{V_n}{4}\right)^{3/2}=17.74\times10^{-7}\left(\frac{L}{M}\right)^{1/2} N^{5/2}V_n^{3/2} \qquad (29)$$

or less, depending on the particular value of u taken. N and V_0 are the constants in Townsend's equation, and are determined for a number of gases. V_0 is approximately, though not exactly, equal to the ionizing potential of the gas. L is the mean free path of the positive ion, which is known to be approximately equal to the mean free path of the molecule or[6] somewhat larger, so if L were considered as the mean free path of the molecule the values given for j_n would come out somewhat smaller than the true values, but would indicate approximately what the true value should be. M is the molecular weight of the gas in the tube.

Thus the constants in Eqs. (28) and (29) are all known more or less approximately, and the values of pd_n and j_n/p^2 must check the empirical results without the use of any adjustable constant.

The numerical data available[7] to check these equations are rather fragmentary and inaccurate. It is possible, however, to make numerical checks on all three Eqs. (27), (28) and (29).

From Eq. (27), V_n depends on D, which depends only on the gas, and on $1-c$, which depends mainly on the cathode material used, though some gases might affect its value. However it is to be expected that the ratio between the V_n's for the same gas but for two different cathodes will be approximately equal to the ratio between the V_n's for a different gas and for the same two cathodes. And similarly for the ratios between the V_n's for the same cathode and for two different gases.

These ratios for observed V_n's are given in Table I.

TABLE I.

V_n for N_2	for Fe	Al	Mg	Pt	Ag	Cu
V_n for He	1.56	1.57	1.60	1.50	1.56	1.50
V_n for A	for Fe	Al	Mg	Pt	Ag	Cu
V_n for H_2	.60	.58	.64	.55	.57	.57
V_n for Fe	for H_2	N_2	O_2	He	Ne	A
V_n for Al	1.21	1.14	1.13	1.14	1.20	1.22
V_n for Mg	for H_2	N_2	O_2	He	Ne	A
V_n for Pt	.63	.83	.81	.78	.72	.73

This indicates that Eq. (27) is fairly correct, even though we have no means of determining the actual values of D or $1-c$.

[6] R. B. Kennard, Phys. Rev. **31**, 423 (1928).

[7] Bär, Handbuch der Physik (Springer) XIV, pp. 190–210.

Using the observed values of V_n, and the known values of the other constants, we can calculate pd_n and $j_n^{1/2}/p$, as given in Table II. In this table

TABLE II. *Values of pd_n and $j_n^{1/2}/p$.*

Cathode		Fe		Al		Mg		Pt	
Gas		Calc.	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.	Obs.
H_2	pd_n	0.94	0.90	0.85	0.73	0.85	0.70	1.02	1.03
	$j_n^{1/2}/p$	.264	—	.23	.25	.22	—	.32	.30
N_2	pd_n	.38	.42	.36	.30	.36	—	.38	—
	$j_n^{1/2}/p$	.407	—	.37	.37	.35	—	.40	.59
He	pd_n	1.82	1.66	1.77	1.32	1.72	—	1.82	—
	$j_n^{1/2}/p$	.091	—	.082	—	.076	—	.091	.10
A	pd_n	.338	.35	.31	.29	.32	—	.35	—
	$j_n^{1/2}/p$	.26	—	.22	—	.23	—	.29	.35

p is in mm Hg; d in cms; j_n in milliamperes/cm². These values check within the limits of accuracy of the measurements, and within the range of variation of results from different observers. We can therefore conclude that our approximations have not been too inexact, and that Eqs. (28), (29) and (30) represent, to sufficient accuracy, the normal cathode fall space.

It is of interest to note the similarity of these results with those obtained by disregarding Poisson's equation and considering that the potential fall distributes itself across the fall space so as to produce the greatest current possible,[5] as in the previous paper by Compton and Morse. The equation for j_n/p^2 in that paper is practically identical with Eq. (30) above, and the similarity between the exponents has been noted earlier in this paper. The expression for pd_n is different, but in that paper the distance d_n was more or less arbitrarily chosen, whereas in the present case pd_n is more or less naturally defined. Moreover the formulas in the present case fit the data somewhat better, and show that V_n *must* be a constant, whereas in the earlier paper this had to be assumed constant.

However, it is interesting to see that in this case a distribution of potential so as to give maximum current is equivalent to a distribution of potential so as to satisfy Poisson's equation.

THE ANODE FALL

By a similar process, the drop in potential at the anode can be calculated. Since no positive ions are emitted by the anode, n_2 at the anode must be zero. The equations become, if L is the distance from cathode to anode

$$n_1=\frac{A}{a+1}\left[a+\epsilon^{2pN(x-L)/3}\right]; \qquad n_2=\frac{A}{a+1}\left[a-a\epsilon^{2pN(x-L)/3}\right] \qquad (30.5)$$

where A has the same value as that given in Eq. (15).

If the anode area is equal to the cathode area, and the current is such that the whole of the cathode is covered with current, *i.e.*, the cathode space

is abnormal, then the current densities at the two electrodes must be equal, and

$$E=\frac{8}{3}DpN\left[(1-c)(1+E_a)+\frac{\epsilon^{2pN(x-L)/3}}{a+1}-\frac{1}{a+1}\right] \tag{31}$$

This indicates that E at the anode equals E at the cathode.

This must be so, for

$$\int_0^L (dE/dx)dx=4\pi e\left[\int_0^L n_1 dx-\int_0^L n_1 dx\right]$$

$$=E_L-E_0=4\pi e[(\text{total no. of electrons})-(\text{total no. of pos. ions})]$$

But for the tube as a whole to be neutral the total number of electrons must equal the total number of positive ions, and therefore E at the anode must equal E at the cathode, as long as the discharge covers the same area at the anode as at the cathode.

These equations indicate that the concentration of positive ions at the cathode is a times the concentration of electrons at the anode.

Since there is no emission of positive ions from the anode, and no necessity for their emission, since they do not create ions, the ratio between bombardment and emission, which fixed the minimum, or normal values of the cathode drop, is not present at the anode, and so there is no analogous normal drop here. The field at the anode therefore reduces continuously as the current is diminished. This means that when the cathode fall is normal, E at the anode is less than E at the cathode. This is not contrary to the previous statements, for in the normal case the current does not cover the whole of the cathode, and we must integrate over a different cross section at the cathode than at the anode. This makes the ratio of the number of lines of force per square cm. (*i.e.*, the field) at the cathode to that at the anode equal to the ratio of the area of the anode to the area of the patch of the cathode carrying current.

Thus the anode drop is not at all as important as the cathode drop. The fall in potential across it is much smaller than the cathode fall, and the concentration of electrons at the anode surface is only $1/(1+a)$ of the concentration of positive ions at the cathode.

The above analysis gives an approximate solution for the two portions of the usual glow discharge tube where the field is large, when electrons are emitted from the cathode by positive ion bombardment.

If electrons are emitted from the cathode by other means, there no longer exists the constancy of the ratio $c/(1-c)$, and, except in the case of very slight electron emission, there is no longer a normal cathode fall space.

For large pressures, and values of E large enough to make z equal to unity throughout the whole discharge, the equations become

$$n_1=A+\frac{A}{a}\epsilon^{2pN(x-L)/3}-A(1-c)\epsilon^{-2pNx/3}$$

$$n_2=A-A\epsilon^{2pN(x-L)/3}+aA(1-c)\epsilon^{-2pNx/3}$$

where c is proportional to the electron current from the cathode. The current will be J times as great as the normal current density, where, if I is the actual current density

$$I=\frac{4}{9\pi}\left(\frac{8}{3}\right)^{1/2}D^{3/2}p^2N^{5/2}uJ$$

from Eqs. (27) and (29). Since we know n_1 at the anode, and the current density at the anode, we can find the field at the anode: $E=(8/3)DpNJ^2$ This determines the constant of integration, in the general equation for E, and V across the whole discharge is

$$V=4D(1-c)+\frac{8}{3}pNDLJ^2+\frac{4D}{1+a}-\frac{8}{3}\frac{pNDL}{a+1} \tag{32}$$

In a gas filled tube containing a filament emitting enough electrons so that positive ion bombardment would not appreciably affect the electron emission, c will remain constant, and V will increase as J increases, until an arc is struck.

In the ordinary electric arc, c is dependent on the current density, represented by J, and will in general increase rather rapidly as J increases. This is obvious from consideration of any of the suggested mechanisms of electron emission from the arc cathode. Therefore as the current is increased V will decrease, until a certain point is reached where further increase in current density causes no further increase in c, either because this excess energy is all radiated away or because the material melts, or for some other reason. At this point a condition very analogous to the normal cathode drop will be in effect, with a constant current density, and a constant potential drop across this space, which, of course, will be much smaller than the normal potential drop for glow discharges. Any further increase in the total current simply increases the area of the "hot spot."

This is exactly what happens in striking an electric arc by passing beyond the condition of a glow discharge. As the current increases from zero, the voltage drop across the discharge decreases, until a "hot spot" forms. Here there is a discontinuity in the curve, and after that the voltage drop at the cathode is independent of the total current. Thus the conditions in the hot spot of an arc, which represent the maximum possible current density in a gas discharge, are quite similar to the conditions in the normal cathode fall in a glow discharge, which represent the minimum possible current density; and this similarity illustrates the essential identity of the equations for arc discharge and for glow discharge.

The Positive Column

The most of the length of the discharge tube, from the anode out to near the cathode, is filled with a luminous portion of the discharge, called the *positive column*. Throughout its length the field has a comparatively constant value E_p. Between certain limits of pressure and current the column is divided into alternate striations of nearly equal distance apart, and having

their greatest intensity near the cathode. When this is the case E_p has imposed upon it a slight sinusoidal variation about its average value, having a wave-length l equal to the distance between striations.

While the data on this portion of the discharge are nearly all qualitative, there are some approximate empirical relationships which have been found. E_p is directly proportional to the pressure and inversely proportional to r the radius of the discharge tube, if the tube is approximately cylindrical. It decreases slightly with increase of total current through the tube. Similarly l varies inversely as p, directly as r, and decreases slightly with increasing current. The potential drop from one striation to the next is proportional to some critical potential of the gas. For the noble gases and the monatomic vapors it apparently equals the first radiating potential, while for molecular gases it is proportional to the ionizing potential.

Examining Eqs. (8) and (9), we see that for E to be a constant, n_1 must, on the average, equal n_2 and this value, call it n_p, must also be a constant. Therefore just as many ions are created per cm according to the first term, as disappear, according to the second term. That is:

$$aNpzn_1E_p^{1/2}=Rp^{1/2}$$

But for small values of E, z becomes approximately $E/\epsilon pNV_r$ where ϵ is the base of the Naperian logarithms. Then

$$\frac{a}{\epsilon V_r}n_1E_p^{3/2}=Rp^{1/2} \tag{33}$$

R is the number of ions disappearing per second per cc. This is probably due principally to recombination of the ions at the walls of the tube. Then the total current going to the walls per cm length of tube is: πr^2eR. Call it J_r. Schottky[3] has found that

$$J_r=i\cdot\frac{2.4}{r}\left(\frac{\chi}{V_r}\right)^{1/2}D_a^{1/2}$$

Here i is the total current flowing along the column, χ is a constant, having values between .4 and .1 for most tubes, and D_a is a sort of diffusion constant proportional to the product of the actual speeds of the electrons and positive ions, and therefore inversely proportional to the product of their respective mobilities. r is the radius of the discharge itself, which equals the radius of the tube, unless the tube is too large; that is, r equals the radius of the tube until this radius reaches a certain maximum value, after which r is constant, no matter what greater radius the tube may have.

Obtaining a value for i in terms of n_1, and substituting all this in Eq. (33).

$$E_p=2.4\epsilon\,(\chi V_rD_a)^{1/2}$$

But Schottky, by other means, obtained

$$E_p=\frac{2.4}{r}\,(V_rD_a/\chi)^{1/2}$$

This means that $\chi = 1/\epsilon r$. For tubes usually used in experimental work r varies from 1 to 4. Therefore χ would vary from .37 to .09, which is the range of variation which has been experimentally determined. D_a, we have seen above, is inversely proportional to the square of the mobility, or by Eq. (6) $D_a = GpE_p$, where G is a constant. Substituting this, and solving for E_p, we find

$$E_p = 5.76\epsilon V_r Gp/r \tag{34}$$

V_r was defined by Schottky as the ionization potential of the gas, but if cumulative ionization takes place, especially if metastable atoms are easily formed, V_r may well be the first critical potential, or one near it.

This value of E_p satisfies the empirical conditions for its dependence on r and p. With increase of current the chances for the same proportion of this current to reach the walls and recombine is probably less, and therefore the value of E_p required to replace this lost proportion of current will be slightly less. This explains why E_p decreases slightly with increase of current.

While E_p and n_p must be, on the average, constant, it may be that they can vary slightly about these as mean values. Set $n_1 = n_p - n$; $n_2 = n_p + n$, where n is small compared to n_p. Solving Eq. (8) for n, assuming that the first two terms cancel each other,

$$n = B\epsilon^{-Ep/2D} \sin\left[\left(\frac{8\pi e n_p}{D} - \frac{E_p^2}{4D^2}\right)^{1/2} x\right] \tag{35}$$

where B is small compared to n_p, and $E_p/2D$ is very small.

This substituted in Poisson's Equation can be integrated to give a similar expression for the variation of E about E_p. It can be seen that this fluctuation is only possible between certain limits of pressure and current. Also, due to the exponential term, the fluctuations are greatest near the cathode, and diminish as the anode is approached.

If it is assumed that the first term under the radical is much larger than the second, then the distance between striations will be $l = 2\pi(D/8\pi e n_p)^{1/2}$. The value n_p is probably proportional to the n_1 or n_2 at the beginning of the anode drop. However, the discharge has now spread out to fill the tube, consequently n_p is also inversely proportional to the square of r, and from Eqs. (30.5) and (15)

$$n_p = \frac{4kDp^2N^2}{9\pi r^2 e(a+1)}$$

where k is a constant dependent on the gas, and perhaps on the particular tube. When this value of n_p is substituted in the equation for l, it becomes

$$l = \frac{3\pi r}{2pN}\left(\frac{a+1}{2K}\right)^{1/2}$$

The potential drop between striations is

$$lE_p = 8.64\pi\epsilon G[(a+1)/2k]^{1/2}V_r = KV_r \tag{37}$$

The coefficient K is independent of p and r and of current, over a considerable range of values, and it may quite possibly be unity for the noble gases. For other gases K assumes other values; while evidently V_r is the first critical potential for monatomic gases, and the ionizing potential for other gases. This would then correspond to the empirical facts.

Thus Eqs. (34), (36) and (37) show that E_p, l and lE_p in their dependence on r, p and V_r, satisfy the empirical facts; hence we can assume that these equations represent approximately the conditions on the positive column.

An explanation of the variation in light can be explained as follows. For each field, the electron will have an average random motion, and an average energy of motion. At a point where E, in its fluctuations about E_p, increases to such a value that the average energy of the electrons is sufficiently near to a radiating energy of the gas molecule, the gas becomes luminous, and some of the excited atoms are ionized. It is not necessary that a great portion of the excited atoms be ionized, for the current through the tube is determined by other means. When E reaches such a value that the electron energy is sufficient to excite another line, this line also appears.

The Faraday Dark Space

At the end of the cathode fall E is zero, or even slightly negative. In this case Eq. (8) can be shown to reduce to:

$$aDd^2n_1/dx^2 = pR'n_1/r = aDb^2n_1$$

for the mobilities used here must be those for a small field as in Eq. (7). This gives

$$n_1 = A\epsilon^{-bx} + n_p\epsilon^{b(x-d)}$$

$$n_2 = aA\epsilon^{-bx} + an_p\epsilon^{b(x-d)} - (a-1)A + (a-1)(A-n_p)x/d$$

where x is zero at the beginning of the dark space, and is d at its end, where the positive column begins. If we solve for E in the usual way, and set E equal to E_p when x equals d, we find that $d = (r/pR')\ (1+k/p)$ where k is dependent on the current density in the positive column. This equation is only very approximately true, for E does not equal zero throughout the dark space, but it serves as an indication of the dependence of d on r, p and the current going through the tube. It checks qualitatively with the experimental data on the width of the dark space.

Conclusion

Thus Eqs. (1), (8) and (9), when solved, account for all the varied phenomena of electric discharge through a gas under different conditions, and what little numerical data is available seems to check these solutions. A set of curves for n_1, n_2 and E for a usual glow discharge, as calculated from the equations given, is shown in Fig. (1).

If we assume that above a certain field E_1 the atoms which are struck by electrons will radiate light, and that above E_2, where E_2 is greater than E_1, the atoms struck will not radiate, but will be ionized, then we can draw two parallel lines across this set of curves, and assume that between these two lines the gas becomes luminous, and above and below them it is not. In this way we can approximately foretell the luminous portions of the tube.

At both ends of the tube a current of many high speed ions is spread more or less evenly over the active portion of the electrode, the ions moving normally to the electrode. As we get further and further from the electrode, the current tends to be carried by a few, low speed ions which tend to concentrate along the center of the tube.

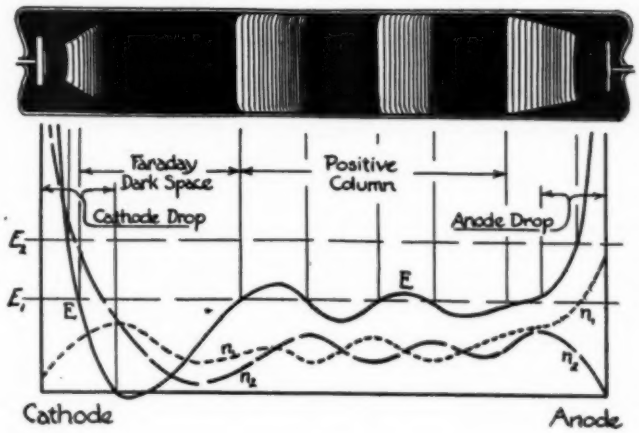

Fig. 1.

The ions required to carry the current to the electrodes are nearly all formed in their respective falls of potential, quite near the electrode for which they are destined. The extra ions of opposite sign are pushed away from each electrode, and travel toward the other electrode. These, the electrons from the cathode fall, and the positive ions from the anode fall, must meet and recombine in some part of the tube. In this place of recombination, the values of E, and the two n's will be the smallest of any part of the discharge. This space must be near the cathode, for even if but few electrons get through the space, these few can increase their number by ionization as the field increases, whereas the positive ions getting through a similar depression near the anode could form no ions, and the discharge would stop.

It is of interest to note that these solutions would not have been greatly changed if μ had been taken according to Eq. (7), instead of according to Eq. (6).

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IONIZATION IN THE UPPER ATMOSPHERE OF THE EARTH*

By E. O. Hulburt

Abstract

A theory of the ionization of the upper atmosphere of the earth by the ultra-violet light of the sun is developed based on known laws of pressures and constitution of the high atmosphere, ionic recombination, attachment of free electrons to neutral molecules, and diffusion of ions. It is concluded that the solar ultra-violet light is a necessary and sufficient cause of the Kennelly-Heaviside layer, and that hypotheses of other agencies of ionization, such as charged particles from the sun, penetrating radiation, etc., are uncalled for except perhaps in unusual cases. Assuming the solar ultra-violet energy to be that of a black body at 6000°K and using known, or estimated, absorption coefficients of the atmospheric gases for ultra-violet waves below λ1300A which cause photo-electric ionization, the electron curve for the sun overhead, i.e. for high noon in summer in the temperate zone, has a maximum of 3×10^5 electrons per cm³ at a height of 190 km. Below this the ionization can not be calculated exactly, because of the lack of many facts which future laboratory experiments may supply, but a density of 10^4 to 10^5 electrons per cm³, or 10^9 to 10^{10} ions per cm³ (or a suitable mixture of ions and electrons) seems possible down to, say, 100 km. This ionization is shown to explain quantitatively many facts of wireless telegraphy, i.e., the skip distances, overhead absorption coefficients, limiting waves, ranges and the apparent heights reached by the waves. Taking into account the seasonal changes in the upper atmospheric pressures and the altitude of the sun, the electron layer for winter noon is found to have a maximum of 1.42×10^5 at a height 147 km, and the ionization below this is less than the summer values by a factor of 2 or so. After sunset the maximum ionization is found to decrease by a factor of about 6 in the small hours of the morning; below the maximum the decrease is greater. These seasonal and diurnal changes in the ionization are shown to be in agreement with the corresponding variations in wireless wave propagation phenomena.

The potential energy of the daytime ionization in a 1 cm² column of the atmosphere is found to be at least 1 erg and the assumption that less than 1% of this is liberated as light will account for the light of the night sky, or the *non-polar aurora*, as Rayleigh calls it. Due to diffusion of the ions along the lines of magnetic force the upper ionic spray of the ionized layer diffuses to the magnetic poles, concentrates there and causes the *aurora*. Calculation indicates that the *ozone* of the atmosphere is perhaps not directly connected with the foregoing ionization, but is formed by longer wave-lengths of ultra-violet light from λ1300 to 1800A.

THE more important agencies which may conceivably produce the ionization of the upper atmosphere of the earth are the ultra-violet light, α and β particles, all of solar origin, the penetrating radiation of cosmic origin, and the ionizing radiations from terrestrial sources. The last mentioned may perhaps be ruled out immediately because of the fact that the ionization in the lower atmospheric strata increases rapidly with the height for the first few kilometers.[1] The penetrating radiation apparently produces but

* Published with the permission of the Navy Department. Read before the National Academy of Sciences, April 24, 1928.

[1] Hess, Phys. Zeits. **14**, 610 (1913).

few ions, about 1.4 per cm per sec, at the surface of the earth[2] and its ionization at the high levels may be expected to be entirely negligible. Hypotheses of α and β particles from the sun must be regarded as tentative in the extreme, and it is safe to say that no phenomena have yet been discovered which point unmistakably to the existence of such particles. There remains the ultra-violet light from the sun as deserving first consideration, and it is the purpose of this paper to examine the effects of its action in the atmosphere. The conclusion may be stated in advance that the ultra-violet light which may be expected reasonably from the sun produces electron and ion densities in the high atmosphere in agreement with the densities inferred from the data of wireless telegraphy. Further, because the question of the ionization of the high atmosphere is merely a part of the larger subject, the entire physics of the atmosphere, we obtain possibly a new glimpse into problems closely related to it, such as the aurora, the light of the night sky and the ozone. Only a glimpse, however, for many facts bearing on these fascinating questions are yet unknown. The possible effects of the various ionizing agencies have been considered by Swann,[3] Chapman and Milne,[4] Chapman,[5] Elias,[6] Lassen,[7] Benndorf[8] and others. In these investigations several factors such as the attachment of free electrons to oxygen molecules, the diffusion of the ions and electrons, etc., which have been considered important in the present investigation, were neglected entirely. New facts, particularly in the field of wireless telegraphy, and new calculations of the pressures in the upper atmosphere for day and night and for summer and winter have recently become available and have been used in the present calculations.

Data of Wireless Telegraphy

Certain facts of skip distances and limiting waves of wireless telegraphy which are of interest in the present development have been furnished by Dr. A. H. Taylor of the Radio Division of this Laboratory. The skip distances for the north temperate zone for summer noon are 1000, 600, 300 and 200 miles for wave-lengths 16, 21, 32 and 40 meters, respectively. The corresponding skip distances for winter noon are 1350, 730, 400 and 200 miles. The values may be in error by a hundred miles or more because the skip distance varies in an erratic manner from time to time. The values agree well enough with earlier ones[9] which referred to daylight conditions averaged throughout the day and year. The change in the skip distance with the hour of the day is shown in Fig. 1 in which the abscissas are the times of day and the ordinates the relative values of the skip distance. The curves, which

[2] Milliken and Cameron, Phys. Rev., **31**, 163, 1928; Hess, "Die elektrische Leitfähigheit der Atmosphäre und ihre Ursache," 1926.

[3] Swann, Terr. Mag. and Atmos. Elec. **21**, 1 (1916).

[4] Chapman and Milne, Roy. Meteor. Soc., Quarterly Journal **46**, 357 (1920).

[5] Chapman, Ibid. **52**, 225 (1926).

[6] Elias, Zeit. f. Hochfreq. Technik **26**, 66 (1926),

[7] Lassem, Ibid. **28**, 109 and 139 (1926).

[8] Benndorf, Phys. Zeits. **27**, 687 (1926).

[9] Taylor and Hulburt, Phys. Rev. **27**, 189 (1926).

of course are not very accurate, are roughly the same for all the waves below 40 meters. In the early morning hours before dawn the curves have been given a jagged appearance to indicate that at these times the skip distances are so variable and erratic as to defy exact estimation.

The limiting wave-length, defined as the shortest wave which can be used for reliable long distance wireless communication, is 10.5 meters for summer noon, 17 meters for summer midnight, 14 meters for winter noon and 23 meters for winter midnight. The limiting wave is an erratic quantity, and the values, which are averages, are considered to be correct within meter or so.

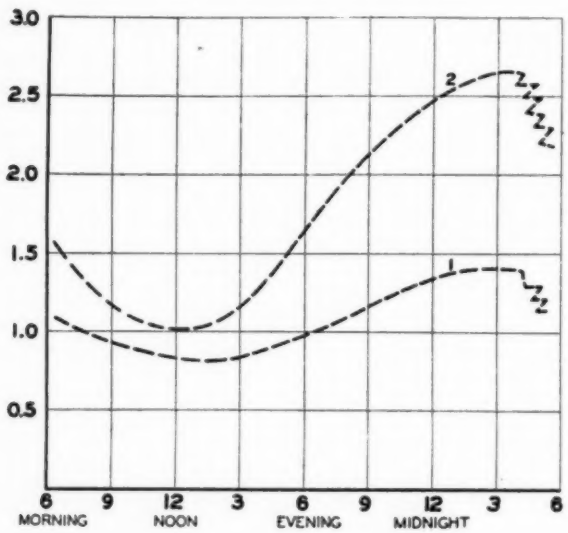

Fig. 1. Relative values of the skip distances of wireless waves below 40 meters in wave-length for temperate zone conditions as a function of the hour of the day, curve 1 for summer, curve 2 for winter.

A number of experimentors have determined the apparent heights above the earth reached by radio waves. Breit and Tuve[10] at Washington, D.C., U.S.A., found that 70 meter waves were reflected (refracted) back to earth at apparent heights from about 90 to 220 km in the daytime in the summer and autumn. Appleton and Barnett[11] determined the apparent heights to be 100 to 130 km for 400 meter waves on a June night in England. Recently Appleton[12] has observed that in the small hours of a winter night these waves seem to pierce their way to 300 or 400 km levels. Heising,[13] at New York City, found that 57 and 111 meter waves seemed to go to heights from 250 to 650 km before being turned back. These experiments were done on

[10] Breit and Tuve, Phys. Rev. **28**, 554 (1926).
[11] Appleton and Barnet, Proc. Roy. Soc. **A113**, 450 (1926); **A109**, 621 (1925).
[12] Appleton, Nature, **120**, 330 (1927).
[13] Heising, Proc. Inst. Rad. Eng. **16**, 75 (1928).

winter nights. Hollingworth,[14] in England, concluded that the apparent heights reached by long waves, 6000 and 14,000 meters, in the day were 75 km in summer and 90 km in winter, the corresponding night values being 10 to 20 km greater. Taylor and Hulburt[9] calculated from the observed skip distances, averaged over the year for daylight conditions, for waves below 40 meters in length, that these waves reach heights between 120 and 240 km.

The Pressures in the Upper Atmosphere

The constituent gases of the outer atmosphere and their partial pressures are taken as given completely in the recent paper of Maris.[15] This paper is a revision and an extension of the classical calculations of Humphreys,[16] Jeans[17] and others and provides tables of the partial pressures of the various gases for summer and winter and day and night. Although the question of the existence of hydrogen can hardly be said to be settled, we follow Chapman and Milne,[4] who have reviewed the evidence, and assume that there is no free hydrogen in the high atmosphere.

We shall need only the values of the total molecular density n (number of molecules per cm^3) and of the density n' of the oxygen molecules. It is convenient to express these as functions of z, the height above the earth in cms, by the relations

$$n = n_0 e^{-pz}, \tag{1}$$

and

$$n' = n_0' e^{-p'z}. \tag{2}$$

The values of p, p', n_0 and n_0' are given in Table I, n_0 and n_0' being the values of n and n' at $z = 60$ km. The equations with the constants of Table I are good approximations for z from 60 to 300 km for day conditions, at night above

Table I. *Constants of equations (1) and (2).*

	p	p'	n_0	n_0'
Summer day	0.872×10^{-6}	0.920×10^{-6}	9.92×10^{15}	2.08×10^{15}
Summer night	1.41×10^{-6}	1.50×10^{-6}	5.08×10^{15}	1.07×10^{15}
Winter day	1.21×10^{-6}	1.42×10^{-6}	5.58×10^{15}	1.15×10^{15}
Winter night	1.47×10^{-6}	1.56×10^{-6}	3.22×10^{15}	6.76×10^{14}

200 km they cease to be very exact. For other heights Maris' tables must be used directly. It is well to mention, as Maris points out clearly enough, that the pressures at heights above 200 km are open to uncertainties of hundreds of percent, for they are based on assumptions of temperatures which may be widely in error.

Disappearance of the Free Electrons

There are three ways in which the free electrons of any region of the atmosphere may disappear, by diffusion into other regions, by combining with positive ions, and by attaching themselves to neutral molecules.

[14] Hollingworth, Journal of Elec. Engrs. **64**, 579 (1926).
[15] Maris, to be published soon.
[16] Humphreys, "Physics of the Air," 1920.
[17] Jeans, "Dynamical Theory of Gases," 1925.

Diffusion. In considering the diffusion of the ions and electrons we assume that *each element of volume of the upper atmosphere is electrically neutral and remains so at all times.* It is true that in the lower atmosphere there is a gradient of electric potential and a vertical electric current, but in the light of the thunderstorm theory of C. T. R. Wilson[18] it seems probable that these effects do not extend to altitudes above, say, 40 km. The charged particles which are produced by the ultra-violet light in equal positive and negative amounts throughout each element of volume, diffuse about to attain if possible their equilibrium pressures. The diffusion of the electrons is considered to be governed entirely by the motions of the positive ions, for because of the electrostatic forces electrons may not stray from any region unless accompanied by equal numbers of positive ions, and, conversely, wherever the positive ions go equal numbers of electrons flock along with them.

The two hypotheses, (a) that all parts of the upper atmosphere are electrically neutral (or, in other words, that the fluctuations of excess charge are restricted to small volumes), and (b) that the profound electrical disturbances of the lower atmosphere around us do not extend to the high atmosphere, are very far reaching, and it must not be supposed, from the brief account that has been given, that their importance has been underestimated. If these hypotheses are untenable probably all the conclusions of the present paper must be modified. At best, I imagine, the hypotheses can only be regarded as approximately true.

If the density of particles of one kind is ρ_1 and of a second kind is ρ_2, and if ρ_1 is much less than ρ_2, the number N of particles of the first kind which move by diffusion across a cm^2 each second in the positive direction of the Z-axis is given[19] to a close approximation by $N=-0.41\gamma u\partial\rho_1/\partial z$ where γ is the mean free path of the first kind of particles, u their velocity of thermal agitation, and $\partial\rho_1/\partial z$ the departure of the pressure gradient along Z from the equilibrium gradient, i.e. the gradient for no diffusion. In the present case we have ions of density y diffusing among the gas molecules of density n, and (as we shall see) y is always less than $10^{-2}n$. There will be no diffusion of the ions if $y=Cn$, where C is a constant; in this case the slope of the ionic density curve is $dy/dz=Cdn/dz=-py$ (from (1)), and the ions may be said to be in uniform mixture equilibrium. If equilibrium does not exist there will be diffusion, and the rate of diffusion of the ions across a cm^2 is

$$N=-0.41\gamma u(-py-dy/dz). \tag{3}$$

This formula also gives the diffusion of the electrons. With a temperature 219°K, $u=10^5$ cm sec^{-1} (actually u is 5.8×10^4, 6.3×10^4 and 1.7×10^5 for oxygen, nitrogen and helium ions, respectively). The mean free path of the ion $\gamma=1/2^{1/2}\pi n\sigma^2$, the molecular diameter σ being taken to be 3×10^{-8} cm. Formula (3) becomes

[18] Wilson, Phil. Trans. Roy. Soc. **221,** 73 (1921); Proc. Phys. Soc. London **37,** 32D (1925); Nature **119,** 502 (1927).

[19] Jeans, "Dynamical Theory of Gases," Ch. XIV, 1904.

$$N=10^{19}(py+dy/dz)/n. \tag{4}$$

The rate of decrease of electrons (or ions) in a unit volume due to diffusion is

$$dN/dz=10^{19}(d^2y/dz^2+2pdy/dz+p^2y)/n. \tag{5}$$

Diffusion of the ions in the magnetic field of the earth. The magnetic field of the earth will have no appreciable influence upon the diffusion of the ions for gas pressures sufficiently high, i.e. above 10^{-8} atmospheres, but for lower pressures it reduces the diffusion across the field. For, an ion of mass m and elementary charge e moving with a velocity u transversely to a magnetic field H goes in a circle of radius r, where r is given by the relation $Heu=mu^2/r$. So that the straight line distance which a free ion can progress across the field can not be greater in order of magnitude than r. This does not disturb the diffusion formulas (4) and (5) as long as the free path γ is less than r, but for $\gamma>r$ we may replace γ of (3) by r as a rough approximation.

With $H=0.5$ gauss and with u corresponding to a temperature 219°K, r is 4×10^2 cm for oxygen and nitrogen molecular ions and 1.4×10^2 cm for helium ions. γ is 3×10^2, 2×10^3 and 10^4 cm at heights of 160, 180 and 200 km, respectively, on a summer day. Therefore, at about 180 km on a summer day and 140 km on a winter day the magnetic field reduces the diffusion of the ions across it by a factor of 5 from its value in the absence of the field, and at greater heights by a greater factor. The diffusion along the field is of course undistrubed by the field. In the present instance we are primarily interested in calculations for the temperate zone where the lines of magnetic force are at 45° or so with the vertical and we are content to neglect the effects of the field on the downward diffusion of the ions even at heights of 200 km (summer day). It seems certain, however, that a portion of the ions formed at greater heights are guided to the magnetic poles and accumulate there. The recognition of this has given a new theory of the origin of the aurora which is described in a subsequent paper.

Recombination of ions and electrons. A theory of the recombination of ions has been worked out by J. J. Thomson.[20] The essential idea of the theory was that an electron, or a negative ion, upon collision with a positive ion would combine with the ion only if the energy of recombination were dissipated in some way, as by the action of a neutral molecule. Therefore recombination involved a sort of three body collision, the energy of recombination going presumably into heat. The theory takes no cognizance of the possibility of recombination with the emission of radiation; this will be discussed later on. If ρ and ρ' are the densities of the positive and negative particles, respectively, the number of recombinations per second per cm³ is

$$A\rho\rho'. \tag{6}$$

A general expression for A was derived by Thomson which, for pressures less than a centimeter of mercury, reduced to

[20] J. J. Thomson, Phil. Mag. **47**, 337 (1924).

$$A = 2\pi(u^2+u'^2)^{1/2}(2e^2/3kT)^3(1/\gamma+1/\gamma'), \tag{7}$$

where u and u' are the velocities of thermal agitation of negative and positive ions, respectively, γ and γ' their free paths among the molecules of the gas, T is the absolute temperature and k the molecular gas constant 1.372×10^{-16} erg deg^{-1}. For free electrons and positive ions $\gamma = 4/\pi n\sigma^2$ and $\gamma' = 1/2^{1/2}\pi n\sigma^2$. The molecular diameter σ is 3×10^{-8} cm for the gases of the outer atmosphere. At the temperature 219°K $u = 10^7$ cm sec^{-1} and u' is around 10^5. Putting these values in (7) gives $A = an$, where $a = 3.82\times10^{-23}$, and as there are equal densities y of electrons and positive ions the rate of their recombination per cm^3 is from (6)

$$any^2 = 3.82\times10^{-23}ny^2. \tag{8}$$

Similarly the rate of recombination per cm^3 of positive and negative ions, of oxygen or nitrogen is

$$a'ny^2 = 5.45\times10^{-25}ny^2. \tag{9}$$

Thomson showed that the general formula for A agreed well with observations at pressures around an atmosphere. As a test at lower pressures (8) gives $an = 1.22\times10^7$ for the recombination of electrons and positive ions in air at room temperature and a pressure of 0.2 mm of mercury, and Rumpf[21] obtained from experiment a value $an = 0.35\times10^7$; the agreement is regarded as satisfactory.

The attachment of electrons to neutral molecules. At the present time a complete theory of the attachment of electrons to neutral molecules or atoms is not available. From the observations of Townsend and Bailey,[22] Thomson,[23] Loeb,[24] Wahlin[25] and others it seems that free electrons in thermal equilibrium at ordinary temperatures and pressures with molecules of the gases of the earth's atmosphere do not attach themselves to any of these molecules, thereby to form negative ions, except to oxygen molecules. Although there is some discussion[26] as to the exact value of the attachment coefficient for free electrons with oxygen molecules, the order of magnitude 10^5 is fairly well agreed to. This means that the electron makes 10^5 kinetic theory collisions with the oxygen molecules before it becomes attached to a molecule. We assume that this value is true for the low temperatures and pressures of the outer atmosphere. The number of free electrons which become attached to oxygen molecules per cm^3 per second is

$$uy/10^5\gamma, \tag{10}$$

where u is the thermal velocity of the electrons and γ their mean free path among the oxygen molecules. Since $\gamma = 4/\pi n'\sigma^2$ (n' is the density of the

[21] Rumpf, Ann. d. Phys. u. Chem. **66**, 55 (1921).
[22] Townsend and Bailey, Phil. Mag. **43**, 875 (1921).
[23] Thomson, "Rays of Positive Electricity."
[24] Loeb, Phys. Rev. **17**, 89 (1921).
[25] Wahlin, Phys. Rev. **19**, 173 (1922).
[26] Bailey, Phil. Mag. **50**, 825 (1925); Brose, Phil. Mag. **50**, 536 (1925).

oxygen molecules, σ their diameter), $\sigma = 3\times10^{8}$ cm and $u = 10^{7}$ cm sec^{-1}, (10) becomes

$$bn'y = 7.1\times10^{-14}n'y. \tag{11}$$

(I have wondered about the correctness of arguments, such as the foregoing, which are based on average values. Better expressions, although perhaps not greatly different, might be expected to come out of Einstein's considerations of fluctuations.)

Ionization by the Ultra-Violet Light of the Sun

Let I_λ be the intensity of the sunlight of wave-length λ at a height z cms above the surface of the earth. If the direction of the light makes an angle ψ with the vertical, then

$$dI_\lambda = \beta_\lambda n I_\lambda dz/\cos\psi, \tag{12}$$

where β_λ is the molecular (or atomic) light absorption coefficient of the gas for light of wave-length λ. (12) is of course the usual definition of β_λ. Putting (1) into (12) and integrating gives

$$I_\lambda = E_\lambda \exp.\ (-\beta_\lambda n/p\cos\psi), \tag{13}$$

where E_λ is the intensity of light of wave-length λ for $z=\infty$, i.e. outside of the atmosphere.

Let $q_\lambda d\lambda$ be the number of ion pairs (i.e. electrons and positive ions) produced per cm^3 per sec by the light in the wave-length region λ to $\lambda+d\lambda$ and let W be the work of ionization of the gas molecule (or atom). Then

$$q_\lambda d\lambda = [\beta_\lambda n E_\lambda \exp.\ (-\beta_\lambda n/p\cos\psi)d\lambda]/W, \tag{14}$$

on the assumption that all of the absorbed energy causes ionization. The total electron production will be $\int q_\lambda d\lambda$, the integral to be taken over all regions of the spectrum which cause ionization. There will be a similar integral for each type of molecule or atom in the atmosphere and a more complete expression for the electron production would be represented by a sum of such integrals. However, too little is known about the photoelectric ionization of gases to permit a complete expression to be dealt with, and therefore we simplify (14) by dropping the subscript λ and write

$$q_z = [\beta n E \exp.\ (-\beta n/p\cos\psi)]/W, \tag{15}$$

where q_z denotes the number of ion pairs, or electrons, produced per cm^3 per sec at a height z. If the light is totally absorbed, or nearly so, in passing down to a height z, the total number of electrons q produced per sec in a 1 cm^2 column which extends from outside the atmosphere to z is

$$q = \int_z^\infty q_z dz = (E\cos\psi)/W. \tag{16}$$

On a simple photoelectric theory of ionization (Bohr's Theory) the light which causes ionization is in that region of the spectrum extending to shorter

wave-lengths from the limit of the principal series. The atomic and molecular absorption coefficients in this region are just beginning to be hinted at in experiment and theory. Ditchburn[27] observed β to be 10^{-18} for potassium atoms and derived a value 10^{-16} for the molecule. Oppenheimer[28] calculated a value 2×10^{-17} for hydrogen-like atoms from a theory based on the new mechanics. For the absorption coefficients of the lines of the principal series values of 10^{-12} are mentioned. It seems that we are justified, as a working hypothesis, in taking β fairly high, equal to or greater than 2×10^{-17}, for that light which is most effective in causing photoelectric ionization. This means that the light will be nearly all absorbed in reaching a 190 km level on a summer day, for above this level there are $\int_{190}^{\infty} ndz = 6.6\times10^{16}$ molecules. The manner in which β varies with λ below the series limit is not known; Milne[29] finds theoretically that it decreases as λ^2 for hydrogenic atoms. For oxygen and nitrogen the processes of ionization of the molecules are not clearly understood. Apparently electron impacts generated by 17 volts or more (corresponding to λ725A or less) are necessary to make any sort of ionization in nitrogen.[30,31] For oxygen about 13 volts (λ950A) are needed to produce ionization, although it may be that by successive steps or cumulative action 10.8 volts (λ1140A) are effective.

If the distribution of energy in the spectrum of the sun be that of a black body at a temperature 6000°K, then with the value 1.35×10^{6} erg cm^{-2} sec^{-1} for the solar constant the energy E in a band $5A$ wide at λ890A falling vertically down on the outer atmosphere of the earth is 4.5×10^{-3} erg cm^{-2} sec^{-1}. (It may be recalled that the energy at the earth's surface of moonlight is 1, of starlight is 3×10^{-3} and of the penetrating radiation is 3×10^{-4} erg cm^{-2} sec^{-1}.) At this wave-length the work of ionization W is 2.23×10^{-11} ergs and therefore from (7) E/W is 2×10^{8} ion pairs. If the ionizing region of wave-lengths is at 1300A the width of the band is less than 0.1A in order for E/W to be 2×10^{8}, and for a region beginning at λ880A the band must extend to $\lambda=0$ for E/W to be 2×10^{8}.

The upshot of all this is; first, it is reasonable to assume that a large part of the ionization is caused by the short wave ultra-violet light, say, below λ1200, whose absorption coefficient in the gases of the outer atmosphere is high, greater than 2×10^{-17}, so that on a summer day most of the electrons are produced above the 200 km level; and second, it is reasonable to assume that the sun emits enough ultra-violet light in the proper region of the spectrum to produce 2×10^{8} ion pairs in the upper atmosphere each second in a column 1 cm^2 extending from 200 km upward to interplanetary space.

The reason for assuming a rate of production of 2×10^{8} ions pairs is that, as is shown later, this yields an ionization in agreement with the data of

[27] Ditchburn, Proc. Roy. Soc. **A117**, 486 (1928).
[28] Oppenheimer, Zeits. f. Physik. **41**, 268 (1927).
[29] Milne, Phil. Mag. **47**, 209 (1924).
[30] Mohler, Nat. Res. Council Bul. **9**, 118 (1924).
[31] Hogness and Lunn, Phys. Rev. **27**, 732 (1926); **26**, 786 (1925).

wireless telegraphy. It must be emphasized, however, that after the laboratory has furnished certain facts of ionization of gases one should, taking the sun's ultra-violet intensity and the atmospheric pressures, etc., as known, be able to calculate the ionization of the upper atmosphere independently of any reference to the facts of wireless transmission. Or perhaps a better point of view is that the facts of wireless may eventually be used to give the distribution of sunlight energy in the extreme ultra-violet.

The electron layer formed by solar ultra-violet light absorbed above the 200 *km level on a summer day.* At any place in the atmosphere the change in the electron density y with the time t is equal to the difference between the rates of production and loss of the electrons. From (5), (8), (11) and (15) we obtain

$$dy/dt = q_s F(t) - 10^{19}(d^2y/dz^2 + 2p\,dy/dz + p^2y)/n - any^2 - bn'y, \qquad (17)$$

where $F(t)$ is a periodic, or rather an intermittent, function of the time. It represents the variation of the sunlight throughout the day and its cessation at night. An exact solution of (17) is not attempted here, we pass immediately to approximations. In the daytime equilibrium of the electron density exists and $dy/dt = 0$. Considering now the case in which all the electrons and ions are produced above the 200 km level and none below this level, (17) for daytime equilibrium becomes

$$10^{19}(d^2y/dz^2 + 2p\,dy/dz + p^2y)/n + any^2 + bn'y = 0. \qquad (18)$$

The y,z curve, i.e. the electron distribution curve, is obtained from (18) by approximate methods; its general shape can be seen from physical considerations. At high altitudes because of the low pressures which make for rapid diffusion and slow loss of the free electrons, the y,z curve will be closely that of uniform mixture equilibrium. Passing to lower altitudes the removal of the free electrons due to recombination and attachment increases very rapidly until the removal predominates over the supply due to diffusion. y therefore increases to a maximum, with z decreasing, and below the maximum falls rapidly to zero, as in curve 1, Fig. 2. More specifically, from some point a, curve 1, upward the curve follows the uniform mixture equation

$$y = y_a e^{-pz}, \qquad (19)$$

which of course is nothing but (18) with all the terms to the right of the parenthesis put equal to zero. Below the point a the curve is drawn step by step from (18) with sufficient precision, by following the course of the first and second derivatives. It is possible to do this because dy/dz is positive below the maximum; hence d^2y/dz^2 is essentially negative and the curve is concave towards the Z-axis. The numerical values of the coefficients in (18) are such as to permit but little latitude in a proper choice of y, dy/dz and d^2y/dz^2 for each value of z in this region.

Turning to the calculations, $\psi = 17°$ for the temperate zone in summer (as at Washington, D. C.). $E/W = 2\times10^8$, as discussed in an earlier paragraph, and therefore from (16) $q = 1.92\times10^8$. The height z_m where y is a

maximum is not known, so we try taking it at $z=190$ km, as in curve 1, Fig. 2, the subscript m referring to the maximum point M. y_m, the value of y at M, is determined from the condition that the total recombination and attachment loss per second from z_m to infinity plus the diffusion downward at z_m is equal to q, or, from (4), (8) and (11),

$$\int_M^\infty a n y^2 dz + \int_M^\infty b n' y dz + 10^{19} p y_m / n_m = q, \tag{20}$$

n_m being the molecular density at M. The integrations in (20) were graphical (or, rather, a portion were), and several trials were necessary before y_m

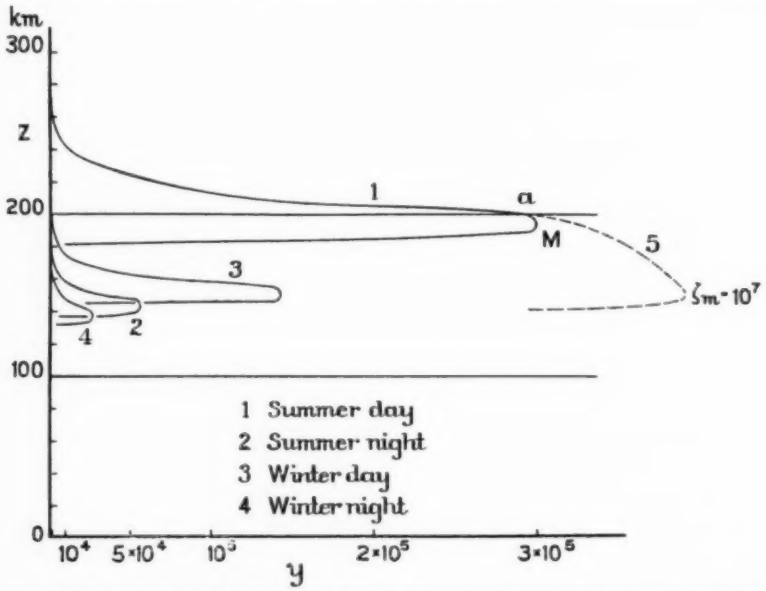

Fig. 2. Calculated ionization curves for the temperate zone resulting from the highly absorbed ultra-violet light of the sun. Curves 1, 2, 3 and 4 give the electron density y as a function of the height z above the earth for a summer day and night, and a winter day and night respectively. Curve 5 is the density ζ of the ions arising from the electrons of curve 1.

was found; it came out to be 3×10^5; the radius of curvature at M was 7.6 km (on the scale of Fig. 2), and the curve followed equation (19) from $z_a=198$ km upwards, with $y_a=2.93\times10^5$. The value of $\int_M^\infty a n y^2 dz$ was 1.1×10^5, of $\int_M^\infty b n' y dz$ was 1.46×10^8 and of $10^{19} p y_m/n_m$ was 4.55×10^7. Below the maximum the curve descended quickly to low values of y at a height of 186 ± 2 km.

Below the maximum the curve must satisfy a relation similar to (20), namely, the total recombination and attachment loss per second must equal the diffusion across the maximum or,

$$\int_{186}^M a n y^2 dz + \int_{186}^M b n' y dz = 10^{19} p y_m / n_m \tag{21}$$

For curve 1, Fig. 2, this relation gave $4.5\times10^5=4.56\times10^5$, which was near enough. Curve 1, therefore, satisfied all the conditions and is the final solution for the distribution of those electrons which are produced at high levels. Furthermore, the curve is the only one which satisfies the conditions for a specified value of q. For, if the maximum was selected higher than 190 km, the diffusion across the maximum was greater than the total loss below the maximum, and if the maximum was taken below 190 km the reverse was true; this is of course to be expected from the physics of the case. The numerical calculations were made with sufficient care to determine the height 190 km within ± 5 km.

If instead of using $q=1.92\times10^8$ we take a different value, say ten times as great or ten times as small, the respective values of y_m are about 4×10^6 and 2×10^4, but the value of z_m remains practically unchanged at 190 km. *Therefore the height where the electron density is a maximum is* 190 *km* (*on a summer day*) *for those electrons which are produced at high altitudes* and is independent of assumptions about the intensity of the ultra-violet radiations from the sun. It depends upon the physical characteristics of the high atmosphere, as might be expected. Furthermore, the position of the maximum is not very sensitive to the numerical values of a and b in equation (18), changing by about 20 km when these are changed by an order of magnitude.

The rather clumsy method which has been used to unravel equation (18) is deservedly open to criticism; a small point in its favor is that it directs attention constantly to the essential physics of the case. An explicit mathematical solution of (18) would be more satisfactory, but graphical or approximate methods would still be necessary to the introduction of boundary conditions such as (20) and (21). As a matter of fact (18), when simplified a little by putting n' proportional to n, was solved as a series; the series although convergent, required the retention of a large number of terms, about 300, for its evaluation, and so was not useful. Dr. G. Breit very kindly showed that after several transformations a solution could be effected in Bessel's functions; this has not been used.

Agreement with the skip distances. The electron density increases very rapidly with the height, as shown by the portion of curve 1, Fig. 2, below the maximum. Therefore, the skip distances of the wireless waves may be calculated approximately as if the waves were sharply reflected at the height of 190 km, using the theory and method of the former paper.[9] The calculated values agree of course with the observed ones, since E/W has been put equal to 2×10^8 in order to secure this agreement.

The electron bank at night in summer. After nightfall the y,z curve is given by equation (17) with the $q_s F(t)$ term put equal to zero. An approximate solution is obtained by assuming that during the night y suffers a proportional decrease at every point of the daylight curve, curve 1, Fig. 2. Because of the cooling of the high atmosphere at night, the height for a given molecular density is lower at night than in the day, and therefore the entire night y,z curve is shifted downward about 50 km below the day curve in summer, the night curve maximum being at 140 km. The total loss of elec-

trons per second due to recombination and attachment above the maximum of the daylight y,z curve is $\int_M^\infty (any^2+bn'y)dz=1.46\times10^8$, which may be written $483y_m$, since y_m is 3×10^5. The loss per second due to diffusion across the maximum is $10^{19}py_m/n_m=4.55\times10^7=152y_m$. The total number of electrons above the maximum is $5.76\times10^{11}=1.95\times10^6y_m$. Then $dy_m/dt=(483+152)y_m/1.95\times10^6$, which gives the value of y_m at any time t seconds to be $dy_m/dt=3\times10^5$ exp. $(-3.25\times10^{-4}t)$, the constant of integration having been determined from the condition that when $t=0$, $y=3\times10^5$. With $t=8$ hours, y_m from this equation is 30. This is too small a value for it results in night skip distances greater than are observed. A decrement factor five times as small as 3.25×10^{-4} is required. The equation is then

$$y_m=3\times10^5 \exp.\ (-6\times10^{-5}t). \tag{22}$$

With $t=8$ hours, i.e. about midnight, (22) gives $y_m=5.6\times10^4$. The summer night curve with this value of y_m is drawn in curve 2, Fig. 2. The skip distances calculated from this curve are twice the day values and are in accord with the observations given in Fig. 1.

The calculation of the decrease of the electrons at night has yielded a decrement factor, which, although apparently five times too great, is of the correct order of magnitude. We may regard this as an indication of the soundness of the theory. A more exact agreement is hardly to be expected in view of the approximate nature of the entire treatment and of the uncertainty in the numerical values of such quantities as the attachment and recombination coefficients. Perhaps the lateral diffusion due to winds, etc., of the ions from the sunlit to the dark areas is important here. As a matter of fact one could decrease the attachment coefficient, readjust things a bit, and obtain an exact, and perhaps misleading, agreement. Certainly the discrepancy can not be taken to suggest an agency, such as α or β particles from the sun, etc., which maintains the ionization during the night.

The electron layer in winter. For a winter day in the temperate zone (as at Washington, D.C.) the angle ψ which the rays of the sun at noon make with the vertical is 63°. With $E/W=2\times10^5$ equation (16) gave $q=9.1\times10^7$. The y,z curve was determined in the same way as was done for the summer day case. y_m came out to be 1.42×10^5 at $z_m=147$ km, and the y,z curve is plotted in curve 3, Fig. 2. The skip distances calculated from this were in agreement with the observed values.

The calculated decrease of the electrons at night was found to be too rapid, just as for the summer night, the decrement factor being again 3.25×10^{-4} which was five times too large. Upon dividing it by 5 the decrement equation became

$$y_m=1.42\times10^5 \exp\ (-6\times10^{-5}t). \tag{23}$$

With $t=8$ hours y_m from (23) was 2.6×10^4 at a height $z_m=135$ km; this y,z curve is plotted in curve 4, Fig. 2. It gave midnight skip distances 2.5 to 3 times the midday values, in entire accord with the data of Fig. 1.

The ion layer resulting from the electrons produced by the highly absorbed ultra-violet light of the sun. In the foregoing calculations of the electron layers we have supposed that there are 1.92×10^8 electrons and positive ions, for summer noon temperate zone conditions, produced per cm^2 per sec in the atmosphere above the 200 km level. These diffuse downward until, as the present theory puts it, at about 185 km there are no free electrons left at all. About 10^5 electrons each second (in a column 1 cm square) combine with the positive ions to form neutral molecules, and the remaining 1.92×10^8 attach themselves to oxygen molecules. Therefore the region above the 185 km level may be regarded as a source of about 2×10^8 negative oxygen molecular ions and 2×10^8 positive ions per cm per second. It is of interest now to follow the course of these ions in their excursions downward, and here we come upon so many gaps in experimental knowledge that speculation is the rule and hypotheses based on facts are the exception. We have thus far avoided specifying just what the positive ions are, but they are probably largely oxygen and nitrogen ions; possibly helium ions are less abundant because of the greater ionization potentials of helium; and there may be argon and other rare gas ions. Some of the oxygen and nitrogen positive ions may be atom ions and some molecular ions, in just what proportion it is impossible to say. No very satisfactory guess can be made as to what happens to the positive and negative ions after they are formed. A number of possibilities may be suggested: direct neutralization may occur, as by the encounter of, say, a negative oxygen and a positive nitrogen ion; the negative oxygen ion may lose its electron by a suitable encounter with a neutral molecule; ionic recombination with the emission of radiation may occur; oxides of nitrogen may be formed, ozone is formed, water vapor may be present and take part as a catalyst in all sorts of reactions; the presence of multiply ionized and excited atoms and molecules may be important; and to all this must be added the influence of the ultra-violet light from the sun of wave-length longer than, say, λ1000A, thus far left out of mention, which pours continually into the high atmosphere. No doubt in this maze of possibilities are to be found explanations of the light of the night sky, the aurora light, the presence of ozone in the high atmosphere, etc.

In spite of the many uncertainties we make an attempt at the calculation of the ion layer and assume that recombination of the positive and negative ions occurs according to the three body collision theory of J. J. Thomson, as expressed by equation (9). Denoting by ζ the density of the positive (or negative) ions, the general equation of the ζ, z curve is similar to (18), and is $10^{19}(d^2\zeta/dz^2+2pd\zeta/dz+p^2\zeta)/n+a'n\zeta^2=0$. A solution of this was obtained by the same approximate methods as were used for (18), and the ζ, z curve was found to have a maximum at about 150 km with ζ_m about 10^7, for a summer day. The curve is sketched in the dotted curve 5, Fig. 2. Below the maximum the curve fell rapidly, within a few km, to small values of ζ. The decrease in the ion bank at night was found to be given approximately by the equation $d\zeta_m/dt=-0.4\zeta_m^2-2.4\times10^{-5}\zeta_m$, which showed that ζ_m decreased by an order of magnitude in 10^5 sec or 28 hours,

a rather slow decrease. The equation was derived on the hypothesis that, as in the case of the electron layer, the source of ions was removed at nightfall. Actually in the ion case the source does not disappear with the sun, the electron layer itself being the source of the ions, and as it contains 5.76×10^{11} electrons it is able to maintain the daytime production rate of 2×10^{8} ions per sec for 2.9×10^{3} sec or 48 minutes. Therefore the decrease of ions at night is even a little slower than was calculated.

An ion layer, such as drawn in curve 5, Fig. 2, with ζ_m about 10^7 at a height of 150 km is too weak to cause an appreciable refraction and absorption of wireless waves even as long as 1000 meters. Such effects, however, unquestionably exist, and we come to the conclusion, perhaps perfectly obvious, that something more is needed than the ionization thus far sketched out. This brings us to the next section.

The ionization below 190 *km on a summer day.* The ionization due to the highly absorbed ultra-violet light, although adequate to account for the skip distances of the wireless waves, is not capable of explaining many other effects, such as the downward reflection of 400 meter waves at heights around 100 km[11] and of 6000 meter waves at heights of 80 km[14], etc. More ionization in the region from 190 to 80 km, referring to summer day conditions, must exist than is indicated by the ion curve 5, Fig. 2. And, although this curve may underestimate greatly the ion density, because it is based on a recombination formula which may not be applicable, it seems reasonable to suppose that there is light which penetrates below 190 km and produces ions and electrons in regions down to 80 km perhaps. Just what light this might be is not certain, probably those wave-lengths near, but not too near, the principal series limits of the atmospheric gases; Hughes[32] inclines to the view that air, free of dust, etc., can only be ionized by wave-lengths shorter than λ1350A. Experiments [33,34,35] show that there is some sort of ultra-violet radiation, probably of wave-length less than λ1250A, which causes fluorescence, and perhaps we may infer ionization, at 4 cms in oxygen, nitrogen and air at atmospheric pressure. On a summer day the atmosphere above 80 km is equivalent to 40 cm, and above 100 km to 6 cm, of air at sea-level pressures. Furthermore, the energy from the sun in the region from λ880 to 1234A is 4.2 erg cm^{-2} sec^{-1}. This is much greater than the energy 4.5×10^{-3} erg cm^{-2} sec^{-1} which was used for the curves of Fig. 2, and although possibly less efficient might be expected to cause considerable ionization.

But here we are nearly at the end of our rope as far as direct calculations from photoelectric effects are concerned; it seems hardly worth while at this time to assume absorption coefficients and intensities of various wave-lengths of light and work out explicit curves of ionization in the region below 190 km. We are content with merely the preliminary step, that is, to point out what ionization will be in accord with wireless and other data, and

[32] Hughes, Report on Photo-electricity, Nat. Res. Council Bul. **2**, 86 (1921).
[33] Hopfield, Phys. Rev. **20**, 573 (1922).
[34] Oldenburg, Zeits. f. Physik **38**, 370 (1926).
[35] Wynn Williams, Phil. Mag. **1**, 353 (1926).

to mention that as far as can be seen now the sunlight is quite capable of making this ionization.

There are required 40 electrons per cm^3 or 2×10^6 ions (nitrogen or oxygen) for normal incidence, and lesser numbers for grazing angles of incidence, to give the downward reflection at heights of 80 or 100 km observed for the long waves.[14] Between the 100 and 200 km levels about 10^4 to 10^5 electrons or 10^9 to 10^{10} ions (or a suitable mixture of electrons and ions) are necessary to explain the various apparent heights reached by the waves in the pulse experiments of Breit and Tuve[10]. The apparent heights above 200 km observed by Appleton[12] and by Heising[13] in certain cases are not regarded as meaning that the waves are returned from any such overhead heights above the earth. These effects seem more readily attributable perhaps to multiple reflections, delayed group velocities over the ray path, etc., and in addition, in the case of Heising, who used a high powered transmitter, to round-the-world signals, to signals reflected from the magnetic pole ion cap, etc. A density of 10^9 or 10^{10} ions in regions where the molecular density may be as low as 10^{12} seems at first sight to be rather high. But perhaps not so, in view of the undoubted efficacy of ultra-violet light in causing ionization and the slow recombinations of the ions at low pressures.

An ionic density of 5×10^9 ions per cm^3 at a level of 110 to 130 km, or 5×10^4 electrons at 130 to 150 km, or a proper combination of ions and electrons at these heights (and fewer numbers at lower heights) will give values of the overhead absorption coefficients of wireless waves in agreement with those observed. The absorption coefficient κ of an electromagnetic wave transversing an ionized gas has been shown, in the notation of a former paper,[36] to be $\kappa=\pi CG/(1/\lambda^2+G^2)$, for propagation in the absence of a magnetic field. For waves below 1000 meters this reduces approximately in the present notation to

$$\kappa=2.1\times10^{-32}ny\lambda^2 \tag{24}$$

for electrons, and to

$$\kappa=2.0\times10^{-38}n\zeta\lambda^2 \tag{25}$$

for ions. From these relations it is seen that 1 electron is equivalent to 10^6 ions as far as absorption is concerned, and at 140 km with $n=4.4\times10^{12}$ and $y=5\times10^4$, from (24) $\kappa=1.2\times10^{-7}$ for 50 meter waves, which means that the intensity is reduced to $1/e$ of its value in going 40 km through the medium. This seems to be about the right value,[36] for only a portion of the ray path lies in the region of absorption. An ion density of $\zeta=10^9$ at $z=120$ km, where $n=2.57\times10^{13}$ gives about the same absorption.

Calculations based on the recombination and diffusion formulas indicate that ionic densities of 10^9 or 10^{10} in the region from 100 to 190 km (summer day, or 80 to 150 km for a winter day) may be expected to decrease by an order of magnitude or so at night, thereby causing a marked diminution of the overhead absorption, particularly of certain wave-length regions of

[36] Hulburt, Phys. Rev. **29**, 706 (1927).

the wireless waves. However, it is not necessary to enter into further detail to indicate that this sort of ionization may cause an absorption and a refraction of the wireless waves which varies with the wave-length in such a manner as to account in general for the diurnal and seasonal variations of the wireless wave propagation phenomena. This has already been blocked out to some extent in the earlier paper,[36] and, indeed, the idea is now common property of many writers on the subject.[37] Eckersley[38] has suggested that the skip distance is to be attributed to the overhead absorption of the ray and not to the electron limitation hypothesis of the present and earlier[9] papers, but has not put his suggestion into a sufficiently quantitative form to enable it to be tested. Besides, the Radio Division of this Laboratory has experimental evidence (Taylor and Young, Proc. Inst. Rad. Eng., May, 1928), which is regarded as unfavorable to the suggestion.

Finally it may be remarked that the addition of, say, 10^5 electrons or 6×10^9 ions at 150 km to the summer day ionization of curve 1, Fig. 2, lessens the calculated skip distances by only 10 or 20%. Therefore the electron curves of Fig. 2 may be regarded as workable approximations at the present time, although they will undoubtedly require some modification in the future. The possible presence of appreciable numbers of ions amid the electrons may account for Meissner's[39] failure to observe any marked critical behavior of wireless waves in the region of 214 meters, as might be expected, although not necessarily, for an ionization predominately electronic.[9] And yet many polarization experiments, and particularly the recent ones of Appleton[40] and of Hollingworth and Naismith[41] indicate double refractions suggestive of electrons and not of ions.

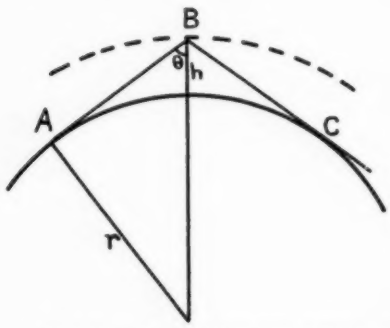

Fig. 3. The limiting ray ABC for sharp reflection from the Kennelly-Heaviside layer.

Limiting waves. A calculation of the limiting wireless wave λ_s for the electron layers of Fig. 2 gives values of λ_s somewhat greater than are observed. For example, referring to Fig. 3, ABC is the limiting ray path and θ is therefore the critical, or Snell, angle of reflection from the electron layer. The refractive index μ of the layer for any state of polarization is very closely for the short waves[9] $\mu^2=1-ye^2\lambda_s^2/\pi m$. Since $\mu=\sin\theta$ (Snell's law) and $\sin\theta=r/(r+h)$, r being the radius of the earth and h the height of the reflecting layer above the earth, we have

$$1-ye^2\lambda_s^2/\pi m=[r/(r+h)]^2. \tag{26}$$

[37] Pederson, Book on Wireless wave Propagation reviewed in the Proc. Inst. Rad. Eng. **16**, 219 (1928).

[38] Eckersley, Journ. Inst. Elect. Eng. **65**, 600 (1927).

[39] Meissner, Elek. Nachr. Techn. **3**, 321 (1926).

[40] Appleton, Proc. Roy. Soc. **A117**, 576 (1928).

[41] Hollingworth and Naismith, Nature **121**, 170 (1928).

Using the summer noon values $h=190$ km and $y=3\times10^5$ we get $\lambda_s=14$ meters. The observed value is 10.5 meters. Similarly with the electron layers of Fig. 2, we find for summer night, winter noon and winter night that λ_s is 24, 18 and 28 meters, respectively, whereas the observed values are 17, 14 and 23 meters.

Upon putting at 150 km an ionized layer of 10^5 electrons or 6×10^9 ions in addition to the 3×10^5 electron layer at 190 km for summer noon, λ_s comes out to be 12 meters. By spreading out the ionization a little in the region below 190 km it is possible to get exact agreement with the observed value 10.5 meters for the summer day case; and similarly for the summer night and winter day and night cases.

Brief summary of the conclusions regarding ionization. Roughly we may say that for summer day conditions in the temperate zone an ionization consisting of about 10^4 electrons or 10^9 ions (or a proper mixture of ions and electrons) at 100 km, increasing to about 5×10^4 electrons or 10^9 to 10^{10} ions at 150 km and 3×10^5 electrons at 190 km, will account quantitatively for many facts of wireless telegraphy, namely, the skip distances, limiting wavelengths, apparent heights reached by the waves, overhead absorptions, and ranges. The calculated seasonal and diurnal variations of this ionization give agreement with the corresponding variations in the wireless wave phenomena. Furthermore, this ionization is in keeping, as far as can be seen, with that to be expected from the action of the ultra-violet light of the sun in the atmosphere. It may therefore be concluded that hypotheses of other ionizing agencies such as charged particles from the sun, penetrating radiations, etc., are quite unnecessary, except possibly (but not probably) to explain secondary or unusual effects such as are indicated in the recent correlations of sunspots and wireless transmission.[42]

Non-polar aurora. There is no evident connection of the negative oxygen ions, formed by the attachment of electrons to neutral molecules, with the night sky light and with the ozone of the upper atmosphere. Except that the green line of the night sky and of the aurora is attributed[43] to the oxygen molecule nothing definite can be said. We may, however, without specifying the exact process* conceive the night sky light, or the "non-polar aurora" as Rayleigh[44] calls it, to come from the solar energy which is stored in the high atmosphere in the form of ionized or excited atoms, and which presumably may be liberated in the form of recombination, or other types of, spectra. This of course is exactly Rayleigh's idea of the night-time "phosphorescence" of the high atmosphere.[45] The recombination formula (7) assumes that all the energy of recombination goes into heat and makes no provision for recombination with the emission of radiation. A complete theory must do this. However, in the present case the amount of radiation

* Cario's recent note, Journ. Frank. Inst. 205, 515 (1928), indicates that the process may be a complex one.

[42] Pickard, Proc. Inst. Rad. Eng. **15**, 1004 (1927).

[43] Cario, Zeits. f. Physik **42**, 15 (1927).

[44] Rayleigh, Proc. Roy. Soc. **A109**, 428 (1925).

[45] Rayleigh, Proc. Roy. Soc. **A109**, 136 (1924).

turns out to be so small as to leave undisturbed the calculations based on (7). The non-polar aurora energy has not been measured, but may be estimated to be 10^{-7} erg cm^{-2} sec^{-1}, or 10^4 quanta cm^{-2} sec^{-1} of green light, at the earth's surface. Taking the total number of electron and positive ion pairs in a 1 cm^2 column of the atmosphere to be 10^{11} as in curve 1, Fig. 2, (there may be many more ion pairs below this curve) and supposing the energy of recombination of each pair is 1.6×10^{-11} ergs (10 volts), there is 1.6 erg stored up, a low estimate. If this energy is shed down as non-polar aurora light at the rate of 10^{-7} erg sec^{-1} only 3×10^{-3} erg are used in 3×10^4 sec or 9 hours. Therefore only a small fraction, less than 1%, of the solar energy stored in the atmosphere as ionization will suffice to maintain the non-polar aurora all night.

Ozone. The energy of formation of ozone is 2.38×10^{-12} erg per molecule, and according to Fabry[46] there are 3.2 mm or 10^{19} molecules of ozone in a 1 cm^2 column of the atmosphere. These persist all night, or at least a sufficient number of them do, to cut off by their absorption stellar spectra at λ2900A; this is also the ultra-violet limit of the sun's spectrum.

Although the process of the formation of ozone by ultra-violet light is not known, let us suppose that the ozone comes somehow from the negative oxygen ions resulting from the attachment of the free electrons which required in summer 4.5×10^{-3} erg cm^{-2} sec^{-1} of the highly absorbed ultra-violet light for their production. The number of ozone molecules formed per sec is, then, $4.5\times10^{-3}\div2.2\times10^{-12}=2\times10^9$, and to produce the 10^{19} molecules observed would take 5×10^9 sec or 150 years, if there were no losses. This seems too long a time; our supposition is therefore untenable, and we turn to other ways of accounting for the ozone. Experiment shows that light in the great oxygen absorption band from λ1300 to 1850A produces ozone, and in this spectral region the sun gives, by calculation, 100 erg cm^{-2} sec^{-1}. This energy would produce $100\div2.2\times10^{-12}=4.5\times10^{13}$ molecules of ozone per sec, and in 2×10^5 sec or 2.3 days the 10^{19} molecules would be made; this seems reasonable. We can go no farther, however, for aside from the fact that light in the ozone absorption band from λ2300 to 2900A causes ozone to revert to oxygen, nothing is known about the life of the ozone molecule or its manner of decomposition. And whether the formation and breaking up of ozone has anything to do with ionization is quite obscure. Oxides of nitrogen, as well as ozone, are formed by the action of ultra-violet light on air, and what part these may play in the physics (or the chemistry) of the atmosphere is entirely dark.

Brief summary of the atmospheric absorption of the ultra-violet light of the sun. In conclusion, a complete theory of the absorption of sunlight in the atmosphere must not be content with showing that some of the light is sufficient to cause the observed ionization, but must account for what happens to all of the light. In Table II are collected various facts and suggestions which have been mentioned in earlier paragraphs. The first column gives the wave-length region in angstrom units, the second column

[46] Fabry, Proc. Phys. Soc. London **39**, 1 (1926).

TABLE II. *The Energy of the sun's ultra-violet light in various regions of the spectrum which is absorbed by the atmosphere of the earth, and the effects produced.*

Spectral region in angstrom units	Solar energy erg cm^{-2} sec^{-1}	Description
0 to 880	4.5×10^{-3}	Highly absorbed; produces the high lying electron and ion layer, at 190 km in summer and 150 km in winter. A portion of the upper spray of this layer diffuses to the magnetic poles and causes the aurora.
800 to 1250	4	Absorbed and produces ions at lower levels, 190 to 100 km in summer, and 150 to 80 km in winter. The potential energy of some of this ionization, and of the higher lying ionization, may be released at night to cause the non polar aurora.
1250 to 1800	10^2	Absorbed by oxygen and produces ozone. Production of ionization doubtful.
1800 to 2300	8.5×10^3	Not known exactly what absorbs this, but oxygen, ozone, oxides of nitrogen, carbon dioxide, water vapor, etc., may contribute. Production of ionization doubtful.
2300 to 2900	3.7×10^4	Absorbed by ozone and may cause some of the ozone to revert to oxygen. Production of ionization doubtful.

the solar energy in this region falling per cm^2 per sec on the atmosphere of the earth calculated on the assumption that the sun radiates as a black body at 6000°K, and the third column gives a description of the effects which the light may produce. The table is of course highly tentative, the description has been written down in the interests of simplicity, whereas a true and complete description will be in all probability immensely more complex.

NAVAL RESEARCH LABORATORY,
WASHINGTON, D. C.,
February 25, 1928.

ON THE ORIGIN OF THE AURORA BOREALIS*

By E. O. Hulburt

Abstract

It has been assumed by Birkland, Strömer, Vegard and others that the aurora is caused by charged particles from the sun which are diverted to the polar regions by the magnetic field of the earth. There are possible objections to this and it is suggested that the aurora is due to ultra-violet light of the sun which produces ions and electrons in the high atmosphere of the earth above 200 km or so. These diffuse along the magnetic lines of force, concentrate at the magnetic poles of the earth, recombine and in some way yield up their energy to form the aurora. The total aurora energy during a strong display is estimated to be 10^{15} erg sec^{-1}, which is in rough agreement with the energy of the upper spray of photoelectric ionization in the high atmosphere indicated by wireless telegraphy.

BIRKLAND, Strömer, Vegard and others[1] have advanced the theory that the Aurora Borealis is caused by charged particles emitted from the sun which under the influence of the magnetic field of the earth are diverted to the polar regions. There their energy is given to the atmosphere and by some process is converted partially or totally into the aurora light. In the theory a difficulty has existed for a long time which, it must be said, has not been very troublesome because of the rather tentative nature of the theory. If the charged particles are α-particles or ions of some sort they do not combine a sufficient penetrating power with a sufficient magnetic deflectibility to explain the height and structure of the aurora,[2] and if they are electrons their penetrating power may be too great.[3] It is the purpose here to give a slightly different explanation of the origin of the aurora energy which seems on the whole more probable and perhaps more reasonable than the earlier views. The idea has come out of a recent theoretical examination of the ionization of the upper atmosphere of the earth.[4] As in Birkland's theory the energy of the aurora is conceived as coming from the sun. It is borne to the earth not by flying charged particles but by ultraviolet light. A part of the ultra-violet light from the sun is absorbed in the high atmosphere of the earth and produces ions and electrons. These charged particles diffuse with little recombination because of the low pressure; during the diffusion there will be always equal numbers of positive and negative charges in each cubic centimeter of the atmosphere, for, due to the electrostatic fields which would arise, no great separation of positive and negative charges can occur. At great heights, above 200 km, say, where the frequency of collision is small, the diffusion of the ions across the magnetic field of the earth is slow compared to the drift along the field, and there will be a rapid migration of the ions to the polar regions and a concentration there. They move to lower levels and recombine setting free their energy of recombination which in some way causes the aurora. Thus the energy of that portion of the sun's ultra-violet

* Published with the permission of the Navy Department.

[1] Vegard, Phil Mag. **23**, 211 (1912); see also Gehrke, Handbuch der Physikalischen Optik, II, 178 (1927).

[2] Vegard, Phil. Mag. **46**, 211 (1923).

[3] Swann, Phil. Mag. **47**, 306 (1924).

[4] Hulburt, Phys. Rev. **31**, 1018 (1928).

light which is absorbed at high levels in the sun-lit regions is transported to the polar regions and reappears (or a portion of it does) as aurora light. The ions may be regarded as being vaporized in the high atmosphere, and distilled along the lines of magnetic force to the poles where they condense to neutral molecules again and yield up their energy of formation as aurora light. Strömer's[5] recent discovery of an aurora which appeared in that part of the high atmosphere directly illuminated by the sun is in keeping with the present ideas, although of course this daylight luminosity may differ in many ways from the night aurora.

A very rough quantitative estimate of the intensity of the aurora illumination was made at Chebeague Island, Maine, during the strong display of August 20, 1927. The greenish arc of the aurora was visible low in the north from which faint streamers emanated southward; shifting clouds of faint luminosity pervaded the northern hemisphere of the sky. A crescent moon was sinking in the west, and I observed that the aurora radiance was slightly weaker than the moonlight. By means of a fluorescent screen and a piece of black glass which transmitted ultra-violet radiations below $400\mu\mu$ the aurora was seen to be no brighter in the ultra-violet than the moon. The ratio of ultra-violet to visible light appeared to be greater for the aurora than for the moon. These observations were taken to mean that the energy of the aurora light was 10^{-2} of that of full moonlight, or 10^{-2} erg cm^{-2} sec^{-1}. The total area illuminated by the aurora was taken to be 10^{-2} of the surface of the earth or 5×10^{16} cm^2. Therefore the total energy of the aurora light upward and downward was $2\times10^{-2}\times5\times10^{16}=10^{15}$ erg sec^{-1}.

In the ionization calculation[4] it has been shown that 4.5×10^{-3} erg cm^{-2} sec^{-1} of ultra-violet solar energy may reasonably be expected from the sun in that region of the short ultra-violet wave-lengths which cause ionization of the oxygen or nitrogen of the atmosphere, and that the ionization which is produced agrees with that indicated by the experiments of wireless telegraphy. The target area of the earth is πR^2 or 1.3×10^{18} cm^2. Therefore the solar ultra-violet energy which falls upon the whole earth and causes ionization is $4.5\times10^{-3}\times1.3\times10^{18}=6\times10^{15}$ erg sec^{-1}. It is reasonable to assume that 10^{-2} of this goes into the high lying ion pairs which move to the polar regions. Therefore an energy 6×10^{13} erg sec^{-1} is available for the aurora under the ordinary solar influence, and in times of sunspot activity may be much more. This is near enough to the value 10^{15} erg sec^{-1}, which was for an unusually strong aurora display, to support the present view.

Because of winds in the high atmosphere of the earth and of variations in the solar radiation due to sun-spots, etc., the ion layer is probably not uniform but is a thing of shreds and patches. Upon drifting to the poles the patches lengthen into streaks and being touched into luminosity form the auroral streamers. But here I must stop, partly to avoid being too rash, but mainly to admit that my contemplation of the aurora has been too limited to give that steadying of ideas which comes only from experimentation.

NAVAL RESEARCH LABORATORY,
February 7, 1928.

[5] Strömer, Nature **120**, 329 (1927).

RADIO TRANSMISSION FORMULAE

By G. W. Kenrick

Abstract

A radio transmission formula is derived by summing the fields due to an infinite number of reflected waves. The problem is rigorously solved for two parallel infinitely conducting planes, and an approximate solution is obtained for two concentric conducting spheres of finite conductivity. The results thus obtained are found to be in accord with those obtained by G. N. Watson in 1919 by the use of spherical and zonal harmonics. The method here employed approximates much more closely to the point of view adopted by recent workers in the radio field and adapts itself more readily to a study of gradually varying boundaries. A modification in the coefficient of the exponential term in the Austin long wave radio transmission formula which alters it from $(120\pi lI/\lambda\rho)\ (\theta/\sin\theta)^{1/2} \exp\ [-0.0015\rho/\lambda^{1/2}]$ to $(120\pi lI/\lambda)\ (3\pi\theta/8\rho h \sin\theta)^{1/2} \exp\ [-0.0015\rho/\lambda^{1/2}]$ is suggested by the analysis and a theoretical justification for the $\lambda^{-1/2}$ in the exponent for the case of long wave transmission is emphasized. The results obtained by the application of the modified formula to the long wave transmission data obtained by Guierre is discussed and an improvement in the agreement found.

EARLY studies of the problem of the propagation of electric waves over the surface of the earth considered the problem to be that of determining the field at any point on the surface of an isolated conducting sphere due to an oscillating doublet located at a given point P on its surface.[1,2] While these investigations were valuable contributions to theoretical optics, they led to a transmission formula giving an attenuation much greater than that experimentally observed. The explanation of the departure is, of course, to be found in the important role played by the conductivity of the Kennelly-Heaviside layer.

Much successful work has recently been carried out with a view to explaining the phenomena of short wave transmission by means of a study of the reflection and refraction of electric waves by ions and electrons in a magnetic field, but less attention has been given to modifications produced in the classical Hertzian solution for the field at a distant point due to an oscillating doublet when multiple order reflections are considered.

G. N. Watson first attacked this problem in 1919[3] and obtained a solution for two concentric spherical shells of finite conductivity and sharply defined boundaries. Dr. Watson's method of attack involved the setting down of Maxwell's equations and an investigation of their solution in terms of series expansions involving spherical or zonal harmonics.

While admirable from the point of view of the mathematician, the method of Watson was too involved to adapt itself to extension to the consideration of the gradually varying conductivity of the upper atmosphere and other

[1] H. M. MacDonald, Proc. Roy. Soc. **A72**, 59–68 (1903); **90**, 50–61 (1914).
[2] G. N. Watson, Proc. Roy. Soc. **A95**, 83–99 (1918).
[3] G. N. Watson, Proc. Roy. Soc. **A95**, 546–563 (1919).

related problems of considerable importance in short wave transmission. For this reason, perhaps, the work of Watson is not frequently referred to by engineers and physicists working in this field, who have adopted the optical point of view of directly transmitted and singly or multiply reflected rays in their further studies of this problem.

A modification in the coefficient of the exponential in Austin's formula, suggested by Watson's analysis, has also apparently escaped attention, because, perhaps, of the fact that it is implicitly contained in Watson's expression for the Hertzian function, rather than explicitly set down in an expression for the field.

Watson's formula involved physical hypotheses which, while far from accurate in the general case, are nevertheless probably adequate to the treatment of long wave communication, from which Austin's formula was originally derived. It is of interest to note that the results obtained by Watson may also be obtained with slight approximation by an application of the optical point of view of reflected rays.

It will be the purpose of this paper to derive an expression for the field between two concentric conducting spheres by a direct summation of the reflected waves and to consider the application of the formula thus derived to the problem of long distance radio communication.

1. Review of Classical Solution for the Oscillating Doublet

The classical problem of determining the field at a point P due to an electronic charge e vibrating at the origin with an electric moment $A \sin \omega t$ (See Fig. 1) gives for the electric and magnetic field intensities at the point P[4]

$$E_\theta = -(\sin\theta/\rho)A\omega^2 \sin\omega(t-\rho/c) \qquad (1)$$

$$E_\rho = 0$$

$$H_\phi = -(\sin\theta/\rho)A\omega^2 \sin\omega(t-\rho/c).$$

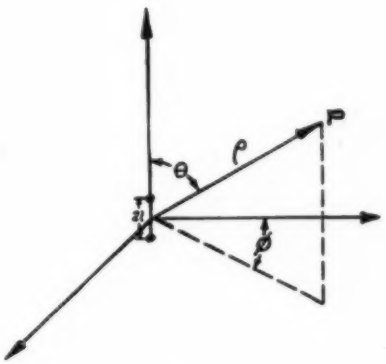

Fig. 1.

It is not unusual, although not strictly rigorous to apply this theory to the case of a radio antenna.[5] Admitting this approximation we evaluate the constant A in terms of the antenna constants.

Thus we may write, where i is the antenna current in absolute electrostatic units, $2l$ the length of the doublet, q the charge, $(2lq = A)$

$$i = \dot{q} = (A\omega/2l)\cos\omega(t-\rho/c). \qquad (4)$$

[4] G. W. Pierce, "Electric Oscillations and Electric Waves." McGraw-Hill, 1920, p. 432 et seq.

[5] Pierce's computations of radiation resistance for flat topped loaded antennae make it possible to correct the results computed on the oscillating doublet theory if such a correction is desired in a particular case. (See text reference, 4).

If I represents the maximum amplitude of i we may write, $2lI = A\omega$ and hence

$$E_\theta = -(\sin\theta/\rho)2lI\omega \sin\omega(t-\rho/c) \tag{5}$$

Noting further that $\omega = 2\pi c/\lambda$ gives

$$E_\theta = -(4\pi clI \sin\theta/\rho\lambda) \sin\omega(t-\rho/c) \tag{6}$$

By the elementary theory of electrostatic images, the field is unaltered by the introduction of a perfectly conducting plane in the horizontal plane $\theta = \pi/2$ (see Fig. 1). The solution given in equation (6) is therefore the solution for the radiation from a doublet antenna of height l located at a point O on a perfectly conducting plane where all quantities are expressed in absolute electrostatic units. For convenience we will let

$$4\pi clI/\lambda = K. \tag{7}$$

At this point it is of interest to note that, expressed in practical units, (amps, kms, volts) this value of K gives for E at the surface of the earth

$$E = 120\pi lI/\rho\lambda \tag{8}$$

where E is the root mean square field in volts/km; I the root mean square antenna current in amps.; ρ the distance in km; λ the wave-length in km; and l the height of antenna in km.

2. Propagation of Waves Between two Perfectly Conducting Planes

We will now alter the conditions of the previous problem by introducing a second perfectly conducting plane at a height h above the $\theta = \pi/2$ plane of Fig. 1 (see Fig. 2). We require the field at a point P on the plane $\theta = \pi/2$ due to the doublet at O.

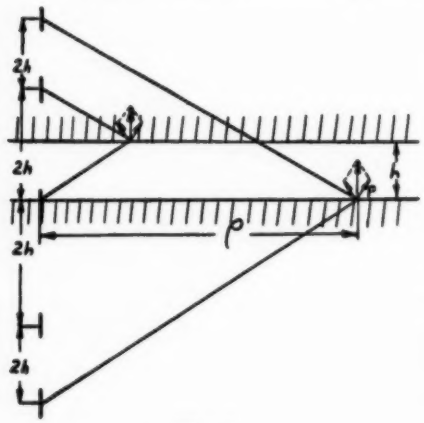

Fig. 2.

We may obtain this solution directly from optics in terms of a direct and a series of reflected rays, but it is perhaps more satisfactory to formulate the problem from the theory of images; i.e. we require a series of image doublets which will cause the tangential electric field at any point on the bounding planes to vanish. Such an infinite series of doublets is indicated in Fig. 2.

The resultant field at the point P is then obtained by taking the sum of the normal components of the electric fields due to each pair of symmetrically located doublets[6] and summing the components due to all the pairs of doublets. This gives for the resultant normal field at P

$$E_p = K\left[\frac{\sin^2\theta_0 \sin\omega(t-\rho/c)}{\rho} + 2\sum_{s=1}^{\infty} \frac{\sin^2\theta_n \sin\omega[t-(\rho^2+4s^2h^2)^{1/2}/c]}{(\rho^2+4s^2h^2)^{1/2}}\right] \tag{9}$$

[6] It will be noted that tangential components of electric force vanish as required.

Noting that $\sin^2 \theta_s = \rho^2/(\rho^2+4s^2h^2)$, this may be written

$$E_p = K\left[\frac{\sin \omega(t-\rho/c)}{\rho} + 2\sum_{s=1}^{\infty} \frac{\rho^2 \sin \omega[t-(\rho^2+4s^2h^2)^{1/2}/c]}{(\rho^2+4s^2h^2)^{3/2}}\right] \tag{10}$$

The evaluation of E_p for ρ/h small may be carried out by direct computation, as the terms in this case rapidly decrease in magnitude. For $\rho/h > 10$ however, this procedure is evidently laborious.

It may be shown, however, that under these conditions the probability is small that the mean E^2 at any point P chosen at random will depart much from[7] $\frac{1}{2}\sum_0^{\infty} E_s^2$ i.e.

$$\overline{E^2} \backsimeq \frac{1}{2} K^2 \left(\frac{1}{\rho^2} + \sum_{s=1}^{\infty} \frac{4\rho^4}{(\rho^2+4s^2h^2)^3}\right) \tag{11}$$

where the units employed are absolute electrostatic units and K is as defined in equation (7).

We will now proceed to some purely mathematical manipulation which may be used to sum this infinite series. We begin by availing ourselves of the well known identity obtainable from product considerations[8] i.e.

$$\coth y = \frac{1}{y} + 2\sum_{s=1}^{\infty} \frac{y}{y^2+s^2\pi^2} \tag{12}$$

Changing the variable by putting $y = \pi x^{1/2}/2h$ gives, after rearranging the terms,

$$\frac{\pi}{4hx^{1/2}} \coth \frac{\pi x^{1/2}}{2h} - \frac{1}{2x} = \sum_{s=1}^{\infty} \frac{1}{x+4s^2h^2}. \tag{13}$$

Differentiating this expression twice with respect to x, multiplying through by K^2x^2, putting $x=\rho^2$ and adding $K^2/2\rho^2$ to each side we have the required summation

$$\frac{1}{2}K^2\left(\frac{1}{\rho^2} + \sum_{s=1}^{\infty} \frac{4\rho^4}{(\rho^2+4s^2h^2)^3}\right) = \frac{1}{2}K^2\left(\frac{3\pi}{8h\rho} \coth \frac{\pi\rho}{2h} + \frac{3\pi^2 \operatorname{csch}^2(\pi\rho/2h)}{16h^2} + \frac{\pi^3\rho}{16h^3} \operatorname{csch}^2 \frac{\pi\rho}{2h} \coth \frac{\pi\rho}{2h} - \frac{1}{\rho^2}\right) \tag{14}$$

Substituting the value of K from equation (7) we may write for the root mean square field E in practical units

$$E = \frac{120\pi lI}{\lambda}\left[\frac{3\pi}{8h\rho} \coth \frac{\pi\rho}{2h} + \frac{3\pi^2 \operatorname{csch}^2(\pi\rho/2h)}{16h^2} + \frac{\pi^3\rho}{16} \operatorname{csch}^2 \frac{\pi\rho}{2h} \coth \frac{\pi\rho}{2h} - \frac{1}{\rho^2}\right]^{1/2} \tag{15}$$

where h is the height of the Kennelly-Heaviside layer in kilometers and the other quantities are in the same units as in equation (8).

[7] This, in the optical analogy amounts to taking the resultant intensity of the light as the sum of its component intensities.

[8] See E. B. Wilson's "Advanced Calculus" p. 454.

For $\rho/h \ll 1$ this equation becomes identical with equation (8) and represents an E inversely proportional to ρ. This is, of course, as it should be as reflected waves will not be of importance at distances from the transmitter very small compared with h.

For $\rho/h \gg 1$, however, the term $(3\pi/8h\rho)$ coth $(\pi\rho/2h)$ governs, and the value of E given by the formula approaches

$$E=(120\pi lI/\lambda)(3\pi/8h\rho)^{1/2} \tag{16}$$

In other words E decreases only with $\rho^{-1/2}$ in this case.

3. Correction for Earth Curvature

In the previous analysis we have found intensity at any point at a distance ρ from an oscillating doublet located at the surface of one of two perfectly conducting planes. This analysis may with slight approximation be extended to the case of two concentric conducting spheres separated by a distance small compared with their radii.

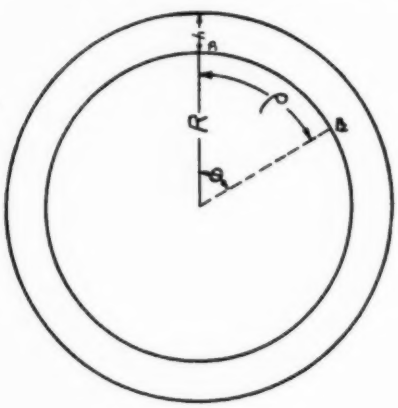

Fig. 3.

Thus, referring to Fig. 3, showing two concentric conducting spheres, we require the intensity of the electric field E normal to the inner sphere at its surfaces at a point P_2 at a distance ρ from an oscillating doublet located at point P_1 on the surface of the inner sphere. If R is approximately 6400 km, and h 100 km, we may to a very good approximation neglect the curvature of the great circle in computing the paths of the rays, thus reducing the problem to much the same form as in the plane case.

It does not follow, however, that we may likewise neglect the curvature of the small circles $R \sin\theta$ or $(R+h)\sin\theta$ on the surfaces of the inner and outer spheres respectively. This results in a focusing action in which the energy flowing out from the emitting doublet passes out, at a distance ρ from the doublet through an area $2\pi\rho h \sin\theta$ as contrasted with an area[9] $2\pi\rho h$ in the plane case. Now the total energy passing through these surfaces[10] must in the absence of attenuation[11] be equal to the total emitted energy of the doublet. If follows, therefore, that for a given ρ if E_s^2 and E_p^2 are the squares of the field intensities in the sphere and plane cases respectively we have with slight approximation[12]

[9] Neglecting higher order terms in ρ/h.

[10] We do not consider waves passing around the sphere more than once. These are not of practical interest because of attenuation.

[11] In case of attenuation factors involving ρ only, this argument is still valid as the same fraction of initial energy reaches the surface at a distance ρ.

[12] Our approximation consists in neglecting certain phase differences, i.e. we assume that $\int_s (E\times H)\cdot ds \backsimeq E^2(\text{area})$. At considerable distances from the transmitter, however, our wave is nearly plane and this approximation is not seriously in error.

$$E_s^2/E_p^2=\rho/R\sin\theta=\theta/\sin\theta.$$

Hence the formula for the mean square field E becomes in this case

$$E_s=\frac{120\pi lI}{\lambda}\left(\frac{\theta}{\sin\theta}\right)^{1/2}\left[\frac{3\pi}{8h\rho}\coth\frac{\pi\rho}{2h}+\frac{3\pi^2\operatorname{csch}^2(\pi\rho/2h)}{16h^2}+\frac{\pi^3\rho}{16h^3}\operatorname{csch}^2\frac{\pi\rho}{2h}\coth\frac{\pi\rho}{2h}-\frac{1}{\rho^2}\right]^{1/2} \tag{17}$$

where the quantities are expressed in km, amp, volts, radians.

For $\rho/h\ll 1$ this reduces to

$$E=(120\pi lI/\lambda\rho)(\theta/\sin\theta)^{1/2} \tag{18}$$

The right hand member of equation (18) is readily recognized as the coefficient of Dr. Austin's transmission formula. Our analysis indicates that when reflections are considered, a more appropriate form of the coefficient for ρ/h would be

$$E=(120\pi lI/\lambda)(3\pi\theta/8\rho h\sin\theta)^{1/2} \tag{19}$$

Figures 4 and 5 give plots of E as computed from equations (18), (19), and (11)[13] for the case $120\pi lI=10^4$ (a constant determined at the transmitting station) $h=100$ km. The interval $\rho=100$ to $\rho=1000$ km is shown in

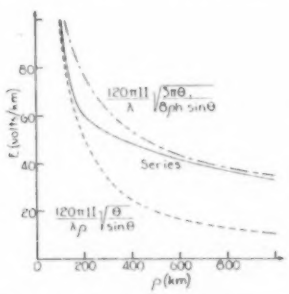

Fig. 4. Comparison of transmission formulae for infinite conductivity case. (ρ small).

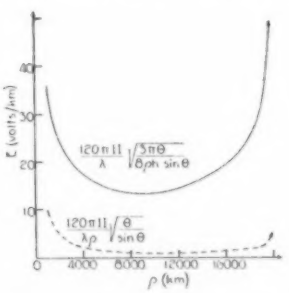

Fig. 5. Comparison of transmission formulae for infinite conductivity case. (ρ large).

Fig. 4 and the interval $\rho=1000$ to 20,000 km is shown in Fig. 5. For values of $\rho<100$ (11) corresponds closely to (18) and for values of $\rho>1000$ to (19).

4. Modifications Introduced by Finite Conductivity

Thus far we have considered the propagation of waves between two perfectly conducting sharply defined planes or concentric spheres. It is not, however, difficult to modify equation (11) in such a manner as approximately

[13] Equation (11) must, of course, be modified to take account of earth curvature and reduced to comparable practical units. This gives for E

$$E=\frac{120\pi lI}{\lambda}\left(\frac{\theta}{\sin\theta}\right)^{1/2}\left[\frac{1}{\rho^3}+\sum_{s=1}^{\infty}\left(\frac{4\rho^4}{(\rho^2+4s^2h^2)^3}\right)\right]^{\frac{1}{4}} \tag{11b}$$

to take into account attenuation due to finite conductivity and non-sharply defined boundary at the upper conducting layer. However, the problem of the summation of the series thereby introduced is not in general as simple as in the infinite conductivity case.

Thus, in the formulation of §2, if we still consider the lower plane (corresponding to the earth) as perfectly conducting, and let r_s be the reflection coefficient of a ray incident on the upper plane at an angle of incidence ϕ_s we have, for the plane case:

$$E^2=\frac{1}{2}K^2\left(\frac{1}{\rho^2}+2\sum_{s=1}^{\infty}\left(\frac{\rho^4 r_s^s}{(\rho^2+4s^2h^2)^3}\right)\right). \tag{20a}$$

It will be noted that §2 was not limited in its application to long distance long wave communication. The approximations of § 3 et seq., however, need further investigation and modification before the above methods can be used to deduce a transmission formula applicable for short wave communication over short or moderate distances. It will in particular be noted that the form of the reflection coefficient of Eq. (20a) distinctly does not hold under these considerations, although the possibility remains of employing a suitably modified coefficient of reflection (or refraction) taking into account the non-metallic nature of the reflector and non-sharply defined boundary.

Another correction of importance when transmission over short or moderate distances is considered arises in connection with the correction for earth curvature. Due to the shadow effect of the earth, according to our approximate treatment, the directly transmitted wave (and, at sufficiently great distances, lower order reflections) would be suppressed. At long distances, the effect of these terms is relatively unimportant. At short distances a term for term computation of Eq. (20a) is possible. If we modify the directly transmitted wave term to the form it assumes in the McDonald-Watson solution for the earth as an isolated conducting sphere Eq. (20a) modified further to take account of earth curvature in the reflection terms, becomes[14]

$$E^2=\frac{\theta}{\sin\theta}K^2\left(\frac{A}{\rho}\exp\left[-\frac{0.0075\rho}{\lambda^{1/3}}\right]+\sum_{s=1}^{\infty}\frac{\rho^4 r_s^s}{(\rho^2+4s^2h^2)^3}\right) \tag{20b}$$

The complete theory of the determination of the quantity r_s as a function of ϕ_s, the thickness of the conducting boundary, and the frequency, involves the entire problem of the wave-length-attenuation function of radio transmission, a discussion beyond the scope of the present article.

It is of interest, however, to note that, on the assumption of an ohmic conductivity and a sharply defined boundary,[15] the reflection coefficient may be approximately written in exponential form.

[14] See references 1 and 2 of page 1. Watson concludes that for this case the Hertzian function is of the order of $(\sin\theta)^{-1/2}\exp[-23.94\theta\lambda^{-1/3}]$ which in our notation is given above. A is a constant.

[15] A boundary may be considered as sharply defined provided reflection takes place in an interval small compared with a wave-length.

From usual optical theory we have, for a wave with its electric intensity vector in the plane of incidence, a reflection coefficient given by[16,17]

$$r_s^{1/2}=\frac{n^2\cos\phi_s-(n^2-\sin^2\phi_s)^{1/2}}{n^2\cos\phi_s+(n^2-\sin^2\phi_s)^{1/2}} \tag{21}$$

where n is the relative index of refraction of the medium, and ϕ_s the angle of incidence.

For a large index of refraction n and a correspondingly large $r_s^{1/2}$, this may conveniently be written by ordinary algebraic division in the form

$$r_s^{1/2}=1-\frac{2(1-\sin^2\phi_s/n^2)^{1/2}}{n\cos\phi_s}+\frac{2(1-\sin^2\phi_s/n^2)}{n^2\cos^2\phi_s}+\cdots \tag{22}$$

or to first order terms in $1/n$,

$$r_s^{1/2}\backsimeq\exp[-2/n\cos\phi_s] \tag{23}$$

For $\rho_1=1$, $\epsilon_1=1$, $\rho_2=1$, and a reflecting medium of specific conductivity γ, n becomes for a wave of period T

$$n=(\epsilon_2+2i\gamma T)^{1/2} \tag{24}$$

For γ large, we have, therefore,

$$|r_s^{1/2}|\backsimeq\exp\left[-\frac{1}{(\gamma T)^{1/2}\cos\phi_s}\right] \tag{25a}$$

Substituting Eq. (25) in (20a), we have, for the plane case, noting that $\cos\phi_s=2sh/(\rho^2+4s^2h^2)^{1/2}$,

$$E^2=\frac{1}{2}K^2\left[\frac{1}{\rho^2}+2\sum_{s=1}^{\infty}\frac{\rho^4\exp\left[-(\rho^2+4s^2h^2)^{1/2}/h(\gamma T)^{1/2}\right]}{(\rho^4+4s^2h^2)^3}\right] \tag{26a}$$

and, from (20b), for the case of the earth as a sphere

$$E^2=\frac{\theta}{\sin\theta}K^2\left(\frac{A}{\rho}\exp\left[-\frac{0.0075p}{\lambda^{1/3}}+\sum_{s=1}^{\infty}\frac{\rho^4\exp\left[-(\rho^2+4s^2h^2)^{1/2}/h(\gamma T)^{1/2}\right]}{(\rho^4+4s^2h^2)^3}\right)\right. \tag{26b}$$

It is of interest to note that in Eqs. (26) the attenuation factor of every term (except that for the ground wave) involves the inverse square root of the wave-length. For lower order reflections and ρ large, moreover, $(\rho^2+4s^2h^2)^{1/2}\backsimeq\rho$. Making this approximation for the series as a whole, the corresponding value of E for the plane case reduces at large distances, in the units of equation (18) (γ measured in mhos/km^3) to

$$E=\frac{120\pi lI}{\lambda}\left(\frac{3\pi}{8\rho h}\right)^{1/2}\exp\left[-\frac{0.183\rho}{h\gamma^{1/2}\lambda^{1/2}}\right] \tag{27}$$

[16] P. Drude's "Theory of Optics" Longmans Green and Co., 1920

[17] Pierce, G. W., "Electric Oscillations and Electric Waves."

Considerations of earth curvature are not essentially altered by the finite conductivity since the exponential factor of attenuation is the same in both cases for equal values of ρ. With earth curvature taken into account (27) becomes

$$E=\frac{120\pi lI}{\lambda}\left(\frac{3\pi\theta}{8\rho h\sin\theta}\right)^{1/2}\exp\left[-\frac{0.183\rho}{h\gamma^{1/2}\lambda^{1/2}}\right] \tag{28}$$

Taking $h=100$ km, an exponent of the order of 0.0015 is obtained for a γ of the order of about one thousandth that of sea water, certainly not an extravagant assumption for the upper atmosphere conductivity.

5. Summary of Results and Conclusions

It thus appears that, under the hypothesis of reflection of the metallic type, an assumption quite possibly justified at long wave-lengths, the inverse square root of the wave-length in the attenuation factor of the original Austin formula has considerable theoretical justification. This theory, however, suggests the desirability of a modification of the inverse first power of the distance in the coefficient of the exponential to an inverse square root. A slight change in the numerical constant in this coefficient is also indicated.

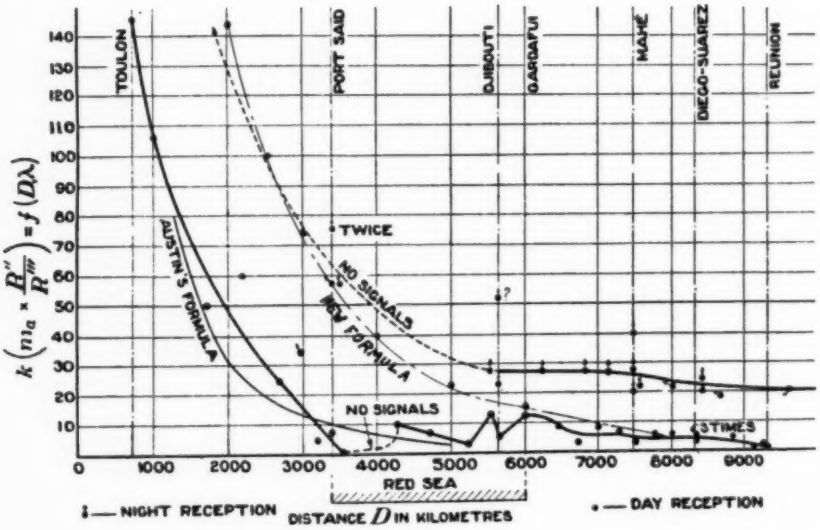

Fig. 6.

The writer has not the data at hand, nor is it within the scope of this paper, to enter into an elaborate statistical comparison of the closeness of accord with experimental data obtained by this formula, the original Austin formula, and a modification recently suggested by Dr. Austin. It will be noted, however, that the above formula gives much larger values than the Austin at large distances where fields predicted by the Austin formula have in general been found to be too small to check with observed results. Some

idea of the relative values of the fields predicted may be obtained from Figures 4 and 5 which plot the coefficients. Let us compare the formula with at least one set of experimental data, however. Figs. 6, 7, and 8 show plots of some

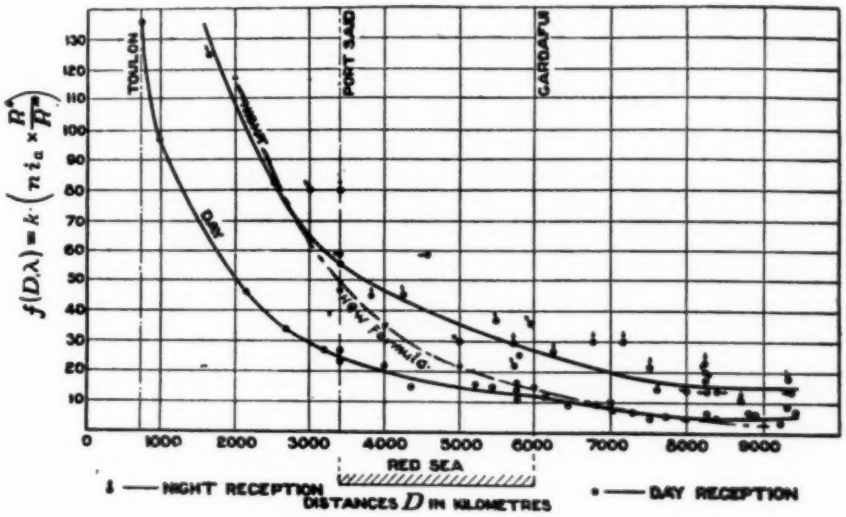

Fig. 7.

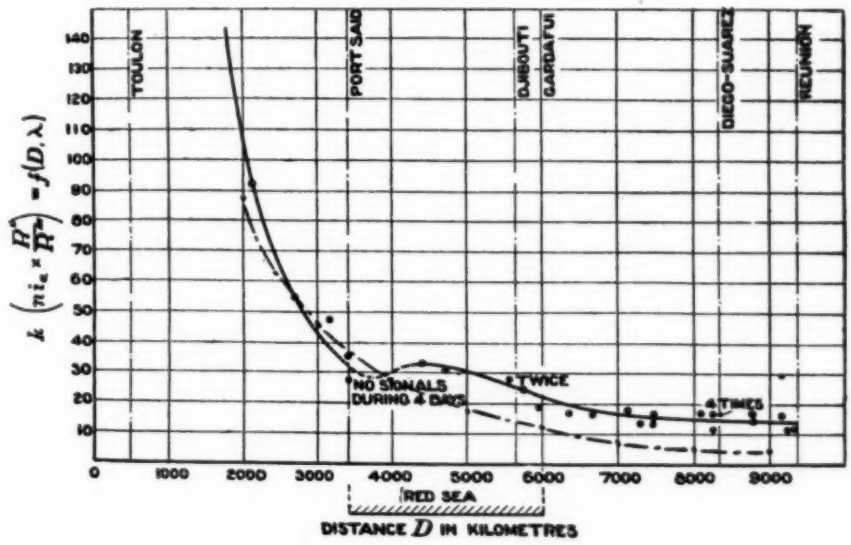

Fig. 8.

of the data taken on the cruise of the Aldebaran to the antipodes.[18] The results obtained from the modified formula are plotted in the broken curves, the remaining curves are reproduced exactly as they appear in Figures 4

[18] "Explorations Hertziennes entre Toulon et Tahiti" Guierre Comptes Rendu de la Societe Francais des Electriciens, 1920, pp. 247–268.

and 5 of the original article. The absolute scale of these curves does not seem to be available. The broken curves were obtained by multiplying the curve for the Austin formula plotted in Figure 4 of the original article by the ratio of the coefficient of the two formulae obtained from this paper. (See for instance Figs. 4 and 5.)

It will be noted that the accord of our formula is distinctly better than that of the original. There is, of course no theoretical reason why the factor 0.0015 in the exponential term should not be subject to modification, and it seems indeed probable that the conductivity of the upper atmosphere is subject to daily and yearly variations. The results of this study indicate the desirability from a theoretical standpoint of seeking modifications in this constant and as indicated in the coefficient rather than in the power to which the wave-length appears in the exponent of the exponential, at least when long distance long wave transmission is under investigation.

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November 15, 1927.*

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APPLICATION OF THE FERMI STATISTICS TO THE DISTRIBUTION OF ELECTRONS UNDER FIELDS IN METALS AND THE THEORY OF ELECTROCAPILLARITY[1]

By Oscar Knefler Rice[2]

Abstract

It is assumed that each atom in mercury is ionized into a positive ion and an electron. Because of the crowded state of the positive ions it is supposed that they cannot move in an electric field, while, following Sommerfeld and Pauli, the electrons are assumed to act like a completely degenerate gas following the Fermi statistics. The distribution of electrons under an electric field due to a charge on the surface of the metal is discussed, and a relation derived which gives the charge on the surface in terms of the potential difference between surface and interior. To a first approximation the charge and potential difference are proportional to each other, as if there were a condenser of constant capacity at the surface. In order to find the capacity an estimate must be made of the dielectric constant of the mercurous ions of the mercury. This is done with the aid of measurements of the refractive index of mercurous ions. The magnitude of the equivalent capacity is such that, when considered in conjunction with the diffuse layer of ions in the solution, electrocapillary curves can be explained.

Introduction

THE distribution of solute ions under the electric field caused by a charge on the surface of the solution was first investigated by Chapman.[3] He used these considerations in an attempt to explain the shape of the electrocapillary curve in the region of its maximum, assuming that the mercury was a perfect conductor so that the charge resided on its surface, while the ions formed a diffuse atmospheric layer in the solution. But, as shown by Frumkin,[4] Chapman's theory did not explain the experimental facts.

Recently the present writer[5] applied Chapman's equations for the distribution of ions to the ions and electrons in mercury, and by assuming that there was a diffuse layer on both sides of the solution-mercury boundary showed that a fair, but still not perfect agreement between electrocapillary measurements and theory could be obtained. These considerations assumed that mercury ions and electrons formed perfect solutes in the mercury, and involved the use of Boltzmann's law for the distribution of ions in the electric field, that is the density of ions (or electrons)at any place in the field was put proportional to $e^{-U/kT}$, U being the energy of an ion (or electron) at a

[1] Read by title at the meeting of the American Physical Society in Berkeley, Mar. 3, 1928.
[2] National Research Fellow in Chemistry.
[3] Chapman, Phil. Mag. (6) **25**, 475 (1913).
[4] Frumkin, Phil. Mag. (6) **40**, 384 (1920).
[5] Rice, J. Phys. Chem. **30**, 1501 (1926).

given place due to the potential of the field, k Boltzmann's constant, and T the absolute temperature. Since it was found that, in order to fit the electrocapillary data, we had to assume that only a small proportion of the mercury atoms were ionized into mercury ions and electrons the assumption of Boltzmann's law appeared to be justified at the time. Indeed, it was to be supposed that it would hold for the electrons to fairly high concentrations, and this fact, it may be stated, would have precluded any attempt to account for the experimental facts by supposing that all the mercury atoms were ionized, but that due to the crowded condition of the positive ions Boltzmann's law could not hold for them.

The writer also showed that the facts could about equally well be accounted for by another theory. In this case it was assumed that the mercury was a perfect conductor, but that between the mercury and the solution there was a condenser of constant capacity, due perhaps to the ions not being able to approach clear to the surface.[6] In the solution itself there was assumed to be the usual diffuse atmospheric layer of ions.

Since the publication of this paper a new proposal has been made in the theory of metals. Pauli[7] and Sommerfeld[8] applied the Fermi[9] statistics to "electron gas" in metals and found that it would be completely degenerate at ordinary temperatures. The latter showed that, on the basis of this theory, contact potentials between metals are given by the equation

$$\phi_2-\phi_1=\frac{h^2}{2m\epsilon}\left\{\left(\frac{3n_2}{4\pi}\right)^{2/3}-\left(\frac{3n_1}{4\pi}\right)^{2/3}\right\} \tag{1}$$

where h is Planck's constant, m the mass and ϵ the charge on an electron, n_1 the number of free electrons per unit volume in the first metal and n_2 in the second, and ϕ_1 and ϕ_2 the potentials of the two metals. By setting n_1 and n_2 equal to the number of atoms per unit volume of the respective metals he obtained contact potentials of the right order of magnitude, though of the wrong sign.[10] On the whole, his considerations seem to indicate that, while the theory may not be entirely correct in detail, its general features have much to recommend them. So we will now reconsider the case of two diffuse layers, using this theory for the diffuse layer in mercury, and the usual one for the aqueous diffuse layer.

Distribution of Electrons at the Charged Surface of the Metal

In the case of electrocapillarity, the electric field in the mercury is produced by an excess of ions of one sign in the solution, which is always balanced by an excess or deficiency of electrons near the surface of the mercury.

[6] Stern, Zeits. f. Elektrochem. **30**, 508 (1924).

[7] Pauli, Zeits. f. Physik **41**, 81 (1927).

[8] Sommerfeld, Naturwissenshaften **15**, 826 (1927).

[9] Fermi, Zeits. f. Physik **36**, 902 (1926).

[10] Sommerfeld did not take into account the difference of the "thermodynamic environment" of the electrons in the two metals. We deal with a single metal.

We will let the excess of positive electricity per unit surface on the solution side of the boundary be Q_0; this is the surface charge for all considerations concerned with the mercury side of the boundary. The potential at the surface of the mercury above that of its interior we shall call ϕ_0; it will have the same sign as Q_0. From our considerations of the distribution of the electrons we shall find Q_0 in terms of ϕ_0. The corresponding relation for the aqueous side of the boundary is known, and the surface tension can be found in the manner described in our previous work.

Near the surface of the mercury, as noted above, there will be an excess or deficiency of electrons, and Eq. (1) must hold for the potential difference between two points near the surface in the same metal, as well as for the potential difference between the interiors of different metals. From it follows immediately

$$d\phi = A\,dn_x^{2/3} \tag{2}$$

where ϕ is the potential (the potential far from the surface being taken as zero) and n_x the density of electrons at a given point, and

$$A = [h^2/(2m\epsilon)] \times [3/(4\pi)]^{2/3} = 1.93 \times 10^{-17} \tag{3}$$

Now we shall assume that each mercury atom gives just one electron. The electrons, being small and freely moving except for the restrictions of the quantum mechanics as shown by Fermi's calculations, will distribute themselves according to Eq. (2). The mercury ions, however, are large and closely packed, and as a first approximation we may assume that their density is the same at the surface as in the interior of the metal. This mass of ions will have a dielectric constant, which we shall designate as K. The density of the ions, which is the same as the density of electrons far in the body of the metal, we shall denote by n_∞. The density of electricity at any point will be given by

$$\rho = \epsilon(n_\infty - n_x) \tag{4}$$

According to Poisson's equation we have

$$\nabla^2\phi = -4\pi\rho/K$$

which reduces in our case (assuming a flat surface, since, as we shall see, the radius of curvature in any practical case will be great compared to the thickness of the surface layer) to

$$d^2\phi/dx^2 = 4\pi\epsilon(n_x - n_\infty)/K. \tag{5}$$

From Eq. (2), $A\,d^2n_x^{2/3}/dx^2 = d^2\phi/dx^2$.
Combining with Eq. (5), $A\,d^2n_x^{2/3}/dx^2 = 4\pi\epsilon(n_x - n_\infty)/K$
By multiplying through by $2\,dn_x^{2/3}/dx$ this equation can be put in the form

$$A\frac{d(dn_x^{2/3}/dx)^2}{dx} = \frac{16\pi\epsilon}{5K}\frac{dn_x^{5/3}}{dx} - \frac{8\pi\epsilon n_\infty}{K}\frac{dn_x^{2/3}}{dx}$$

Integrating from the surface ($x=0$) to $x=\infty$, remembering that at $x=\infty$ we have $dn_x^{2/3}/dx=0$ and $n_x=n_\infty$, and designating quantities at the surface by a subscript zero, we get

$$-A\left(\frac{dn_x^{2/3}}{dx}\right)_0^2=\frac{16\pi\epsilon}{5K}(n_\infty^{5/3}-n_0^{5/3})-\frac{8\pi\epsilon n_\infty}{K}(n_\infty^{2/3}-n_0^{2/3}) \tag{6}$$

Now $n_0^{2/3}-n_\infty^{2/3}=\phi_0/A$ or $n_0^{2/3}=n_\infty^{2/3}+\phi_0/A$. Raising both sides of this equation to the 5/2 power we get (since, as we shall see, $n_\infty^{2/3}>|\phi_0/A|$)

$$n_0^{5/3}=n_\infty^{5/3}+(5/2)n_\infty(\phi_0/A)+(15/8)n_\infty^{1/3}(\phi_0/A)^2+(5/16)n_\infty^{-1/3}(\phi_0/A)^3+\cdots$$

Also $(dn_x^{2/3}/dx)_0=(1/A)(d\phi/dx)_0=-4\pi Q_0/(AK)$. So we see that Eq. (6) takes the form

$$Q_0^2=\frac{3K\epsilon n_\infty^{1/3}\phi_0^2}{8\pi A}\left(1+\frac{1}{6}\,\frac{\phi_0}{An_\infty^{2/3}}+\cdots\right) \tag{7}$$

Now for mercury $n_\infty=4.1\times10^{22}$ per cc so if ϕ_0 is of the order of 0.7 volts or 7/3000 e.s.u. as in the cases we shall dicusss $\phi_0/(An_\infty^{2/3})=0.1$, so that for a first approximation we may neglect the terms after the first in Eq. (7). This means that to a first approximation the diffuse layer in the mercury acts like a condenser of constant capacity given by

$$Q_0/\phi_0=(3K\epsilon/8\pi A)^{1/2}n_\infty^{1/6} \tag{8}$$

and this case reduces to the second one discussed in the introduction, that of a diffuse layer in the aqueous part and a condenser of constant capacity. If we can determine K we can compare the capacity of the condenser with the capacity which best fits the data as found in our previous work.

The Determination of K and Comparison of the Theoretical and Observed Capacities

The medium in which the electrons are dispersed may be considered to more or less resemble a mass of mercurous ions. Accordingly we shall determine K from the mole refraction[11] of mercurous ions. The mole refraction, R, is defined by the following equation

$$R=V(r^2-1)/(r^2+2) \tag{9}$$

where V is the volume occupied by one mole of the substance considered

[11] Pauling, Proc. Roy. Soc., **A 114,** 181 (1927). See especially Eq. (20) of Pauling's article. That the dielectric constant which we calculate is the right one can be seen as follows. If the ions and electrons were point charges in vacuum we would simply have a distribution of electrons and ions in a medium of dielectric constant 1. Actually, however, the ions are polarized in an electric field, and it does not matter whether the electric field is applied from within, as in this case, or from without, as in the case of light going through a crystal. The electrons do not contribute to the dielectric constant, since we are considering a definite distribution of them (i.e., the equilibrium distribution); they are taken account of explicitly in our equations, as is the net charge on the ions. Only the polarizability of the latter, which is the polarizability of mercurous ions, is included in the dielectric constant.

and r is its index of refraction. In a mixture of substances the mole refractions are additive. If the substance is non-magnetic

$$r^2 = K \tag{10}$$

According to Groth[12] the index of refraction of mercurous chloride varies in different directions from 1.95 to 2.60. We take 2.27 as a rough average. Hylleraas[13] finds the density to be 7.21. We then calculate the mole refraction[14] to be 19.00. According to Pauling[15] the mole refraction for chloride ion in crystals lies between 8.04 and 8.48. Taking 8.26 as the approximate value we find the mole refraction of mercurous ions to be $19.00-8.26$ or 10.74. From the known density of mercury we then calculate r^2 or K for the assumed mercurous ions in the metal to be 8.9. Using Eq (8) we find the capacity of the equivalent condenser to be 3.0×10^7 e.s.u., which is equivalent to a plate condenser in vacuum whose plates are of unit area and 2.65×10^{-9} cm apart. In our previous work we found that the condenser which best fits the data would have its plates at a distance of 2.3×10^{-9} cm apart, giving it a capacity of 3.5×10^7 e.s.u.

This quantitative correspondence leads one to believe that the existence of a condenser (for which the evidence is very strong[16]) is probably due to the distribution of electrons in the mercury rather than to other causes, such as the ions in the solution being unable to approach clear to the surface. It may be stated that if the presence of the condenser were due to the latter cause, and we supposed the medium surrounding the ions determined the dielectric constant of the condenser, we find from the dielectric constant of water that the actual distance between the plates of the condenser would have to be about 2×10^{-7}cm—much too large to be reasonable. This may not, however, be a conclusive argument against this supposition, since it is so hard to form a picture of the actual conditions at the surface. We may state, however, that if it is proper to apply Fermi statistics to electrons in metals that some phenomenon such as we have described must occur, and our object is to show that the idealized picture we have presented does give results which agree quantitatively with available data. The various possibilities have not, of course, been exhaustively considered.

In order to get further comparison with experimental data we may perhaps examine the region of the electrocapillary curve where the potential difference is somewhat greater than that considered in our previous paper. It is sometimes unsatisfactory to apply theoretical considerations to the high voltage region of the curve because of the tendency of ions to pile up

[12] Groth, "Chemische, Krystallographie," Wilhelm Engelmann (1906), v. I, p. 215. The values given are for the red lithium line but will not be very different for infinite wave-length.

[13] Hylleraas, Zeits. f. Physik **36**, 861 (1926).

[14] We have arbitrarily used the formula HgCl instead of Hg_2Cl_2. This makes no difference in the final value of the dielectric constant.

[15] Ref. 11, p. 196. We neglect any polarization of the ions with respect to other ions due to movement of the ions as a whole, simply subtracting the value for chloride ion given by Pauling from the value of the mole refraction of mercurous chloride.

[16] At least the diffuse aqueous layer alone cannot explain the facts.

at the surface of the solution. However, according to the present theory, a large part of the potential drop takes place in the mercury. In fact, when the total potential drop between the solution and the mercury is 0.74 volts (fairly high for our considerations) there is only a voltage drop of 0.07 in a solution of 1 N uni-univalent electrolyte. In such a case the concentration of ions of one sign or the other becomes theoretically 16.4 N at the surface. When the total potential drop is 0.46 volts the concentration at the surface becomes 7.4 N. These concentrations are perhaps rather large, but at least the solution is not nearly filled with ions at such concentrations. Besides, most of the lowering of surface tension is due to the mercury side of the boundary where such disturbances do not occur (as may be seen from our previous estimate of $\phi_0/(An_\infty^{2/3})$ or $(n_0^{2/3}-n_\infty^{2/3})/n_\infty^{2/3}$); and the determination of the surface tension involves an integration with respect to potential, including therefore regions where these disturbances do not occur and so somewhat lowering their effect. It is, in fact, my belief, that the capacity of the equivalent condenser determined from the electrocapillary curve in this way is more accurate than that cited from our previous paper.

Krüger and Krumreich[17] decided that of all substances KNO_3 showed the fewest anomalies in its electrocapillary curve. Such anomalies would invalidate the considerations of our previous article in which the calculation of the surface tension due to the combination of the condenser with the diffuse aqueous layer is considered, and since they have only to do with the aqueous side we wish naturally to avoid them for our present purposes. Krüger and Krumreich found with a 1 N solution of KNO_3 an almost perfectly parabolic electrocapillary curve, corresponding to a capacity of 27 microfarads, or 2.4×10^7 e.s.u. We have made calculations, as in our former paper, from 0.0 to 0.741 volts, assuming the equivalent condenser in the mercury to have a capacity as found above of 3.0×10^7 e.s.u. Since most of the potential drop takes place in this condenser we might expect the curve to be nearly parabolic, in spite of the aqueous layer, and it is, within limits of error. When the aqueous layer is included the equivalent capacity of the whole comes out to be 2.7×10^7 e.s.u. The agreement is about as good as we found before. The discrepancy is in the opposite direction. Altogether, the coincidence of the calculated and experimental values is remarkable.

Non-Aqueous Solutions, Etc.

Frumkin[18] finds that for nitrates in methyl and ethyl alcohols and acetone the ascending branch of the curve is parabolic, indicating about the same capacity as in the case of water. This is what is expected, since we believe the electrocapillary curve to be chiefly determined by the mercury. But the descending branch is also parabolic with a shape corresponding to a lower capacity. It thus appears that the thickness of the condenser is greater on the descending than on the ascending branch. It may be that this is to be explained by the presence of an impenetrable monomolecular film of solvent

[17] Krüger and Krumreich, Zeits. f. Elektrochem. **19**, 620 (1913).

[18] Frumkin, Zeits. f. Phys. Chem. **103**, 43 (1922).

which occurs in the descending branch when the mercury is negatively charged, but not when it is positively charged. With aqueous solutions such a film would have to be rather thick to cause an appreciable effect because of the high dielectric constant of water; organic liquids, however, have much lower dielectric constants. Thus there is *a priori* more reason for such an effect to show up in the case of organic liquids than in the case of water. Furthermore, organic liquids wet mercury better than water,[19] which probably means that such a film would be more easily formed. The existence of such a film is supported by Frumkin's data for lithium chloride in different strengths of alcohol.[18] It seems to appear only when the mercury is negatively charged, which may be evidence in favor of the supposition that the more positive portions of the molecules of solvent are attracted to the surface.

Turning to an entirely different case, a curve obtained by von Hevesy and Lorenz[20] with molten lead and molten potassium chloride seems to show a much lower capacity than can be readily accounted for. But such curves have not been exhaustively studied and diffculties and peculiarities would be likely to arise. For example, the capillary electrometer is insensitive and depolarization is great.

Lastly, we may make a remark about the effect of temperature on the ordinary electrocapillary curves.[21] It is small, as would be expected from the fact that Eq. (8), which chiefly determines the effect, according to our theory, has no temperature coefficient.

Discussion

We may now consider some of the points which may be brought against our theory. In the first place, objection may be brought against the application of the Fermi statistics in metals, as being either essentially incorrect or too great an idealization. These questions unfortunately become confused when experimental tests are being made. The use of the Fermi statistics is of course tentative, but, as stated above, there seems to be reason to believe that, for certain purposes at any rate, it can serve as a good approximation. Attempts to develop the theory on more exact lines are likely to lead to complications which will sooner or later necessitate approximations as severe.

We should, of course, take into account the effect of the positive ions on the electrons, but at present it seems probable that at least one electron per atom is comparatively free.[8] If it were necessary to take into account un-ionized atoms, it might be possible for charged positive ions to replace uncharged ones, thus leading to complications.

In our calculations we assumed that the electrons were free to move through the whole space occupied by the mercury. It might be that only a fraction of the space, say f, could be occupied by the electrons. If now n_x and n_∞ retain their meanings as numbers per *total* volume Eq. (4) would remain

[19] Harkins in Bogue's "Colloidal Behavior," McGraw-Hill Book Co. (1924), v. I, p. 177.
[20] von Hevesy and Lorenz, Zeits. f. Phys. Chem. **74**, 454 (1910).
[21] Vining, Ann. Chim. Phys., (8) **9**, 281 (1906).

unchanged since the ρ to be used in Poisson's equation is the amount of electricity per unit total volume. But we should have to replace Eq. (2) by $d\phi = A dn_x^{2/3}/f^{2/3}$. On carrying through the calculations the right hand side of Eq. (8) would be multiplied by $f^{1/3}$, i.e. it would result in the calculated capacity being decreased by a factor $f^{1/3}$, but the effect would not be expected to be important.

Had we made the assumption that each mercury atom was ionized into two electrons and a doubly charged ion our calculations would have been unchanged, but we should have to substitute double the value for n_∞ and an appropriate value of K in Eq. (8). The formula is very insensitive to changes in n_∞ since it appears to the 1/6 power. If, however, we use the value, 3.14, given by Pauling[22] for the mole refraction of mercuric ions, we get a considerably different value for K, and the distance of the plates of the equivalent condenser in vacuum turns out to be 5.2×10^{-9}. This causes us to favor the assumption that there is only one free electron per mercury atom.[23]

Another objection centers around the application of statistical methods to an effect which takes place so near the surface. Actually a layer of molecular thickness is involved.[24] Against this objection may be urged the fact that we wish to consider average conditions at the surface, and that the surface contains many molecules. The method is not an unusual one. We have, of course, neglected surface perturbations, which might be important in so thin a layer. Final decision in these matters must perhaps wait, but the agreement with the electrocapillary experiments is evidence in favor of our method.

GATES CHEMICAL LABORATORY,
CALIFORNIA INSTITUTE OF TECHNOLOGY,
February 25, 1928.

[22] Ref. 11, p. 195.

[23] The note added in proof makes the choice less definite.

[24] The calculation is made as follows. Eq. (8) will hold not only for the surface, but for any point a distance x from the surface. If Q_x includes all the charge between the point x and the surface added algebraically to the charge on the aqueous side of the surface, then

$$Q_x/\phi_x = (3K\epsilon/8\pi A)^{1/2} n_\infty^{1/6}$$

But $Q_x = -(K/4\pi)(d\phi/dx)_x$. So, substituting this value of Q_x, integrating from 0 to x, and taking the exponential of each side we get

$$\phi_x/\phi_0 = \exp\left[-(6\pi\epsilon/KA)^{1/2} n_\infty^{1/6} x\right]$$

The exponent is -1 if x is 2.4×10^{-8} cm, which means that all but a fraction $1/e$ of the potential drop occurs in this distance from the surface. On the aqueous side of the boundary the drop of potential will usually occur in a similar distance.

Note added in proof, April 25, 1928—Since this paper was submitted for publication a more detailed account of the new electron theory has appeared in papers by Sommerfeld and others (Zeits. f. Physik **47,** 1, 33, 38, 43 (1928)). In these articles a correction is made which results in a slight change in our Eq. (1), which now becomes

$$\phi_2-\phi_1=\frac{h^2}{2m\epsilon}\left\{\left(\frac{3n_2}{4\pi G}\right)^{2/3}-\left(\frac{3n_1}{4\pi G}\right)^{2/3}\right\}$$

where G is a weight factor that is given the value 2 to allow for the two spin quantum numbers of the electron. This would cause the right hand side of Eq. (8) to be multiplied by $2^{1/3}$, causing the calculated capacity of the condenser in the mercury to become 3.8×10^7 e.s.u. instead of 3.0×10^7 and the equivalent capacity when the aqueous layer is included to become about 3.25×10^7 instead of 2.7×10^7. This change is in the opposite direction to that which would be produced by correcting for the part of the metal the electrons cannot occupy.

ON THE ACTION OF THE GEIGER COUNTER*

By L. F. Curtiss

Abstract

Experiments performed with a Geiger point counter show that when the point is negative the sensitive surface is on the point, and not on the inner wall of the chamber, as suggested by Kutzner (Zeits f. Physik **23**, 117, 1924). It is further shown that this sensitive surface can only be obtained when the point has been treated in a way which makes it *catalytic*. Such catalysts as iron oxide, copper oxide and platinum black work very well. Their activity is destroyed by catalytic "poisons" such as Hg, SO_2 and H_2S. The experiments indicate that the gas layer usually adsorbed by such catalytic surfaces plays an important role in the action of the counter. The gas layer is demonstrated quite positively by observing the point during operation through a microscope in a darkened room. With a vacuum tube amplifier connected to the counter to actuate a relay at each count, a faint flash on the surface of the point is readily discernible for each click of the relay. When the point is positive no special treatment is needed to make it work. This is shown to be consistent with the explanation offered for the action of the chamber when the point is negative.

THE electrical counter devised by Geiger[1] affords a powerful means of studying phenomena involving individual atoms and electrons. Despite its great usefulness very little is known regarding the real nature of its action. Many attempts have been made to explain its behavior but no one of these explanations possesses the merit of including all observed facts concerning the operation of the counter. There is general agreement that the chamber is in a peculiarly sensitive condition when counting, but conflicting views exist as to the location of the sensitive area, and almost nothing is known or postulated regarding the nature of this sensitive surface. Whereas most observers agree that the point itself must be in a specially activated condition in order to function, Kutzner[2] has suggested that it really is a sensitive layer on the *inner wall* of the chamber which is responsible for the operation of the counter. In any case a theory of the counter must account for a condition such that, when the voltage applied to the chamber is properly adjusted, an α-particle on entering the chamber will start a glow discharge which automatically and almost instantaneously ceases, although the counting chamber is at once restored to its former condition. It is the purpose of this paper to develop a detailed picture of the action of the counter and to describe the experiments which led the writer to this view of its behavior. Since the experiments, which were undertaken in an effort to devise more satisfactory methods of preparing points, preceded an attempt to formulate an explanation they will be described first.

* Publication approved by the Director of the Bureau of Standards of the U. S. Department of Commerce.

[1] H. Geiger, Verh. h. D. Phys. Gessel. **15**, 534 (1913).

[2] W. Kutzner, Zeits. f. Physik **23**, 117 (1924).

In the general absence of definite ideas as to why the counter works, and in particular why one point will work and another almost identical one will not, many methods of preparing sensitive points have been tried. The greatest success has been obtained in the past with platinum and steel points which have been activated by heating in a Bunsen burner. Geiger[3] has called attention to the fact that the action of the counter might be understood if it is supposed that the point has a surface film of high electrical resistance. Acting on this view, the author has prepared points by coating them with insulating and semi-insulating varnishes. These were unsuccessful save in a few cases. Even such points as worked were not reliable. Other substances too numerous to mention in detail were tried. In the course of these experiments a steel needle, coated with metaphosphoric acid, gave very good results. This accidental experience led to the series of experiments which are described.

In order to secure a permanent record of the behavior of the points, a vacuum tube amplifier was used in connection with the counting chamber to operate a chronograph pen. A diagram of the arrangement is shown in Fig. 1. The only novel feature of the two-stage amplifier is the use of a gas-

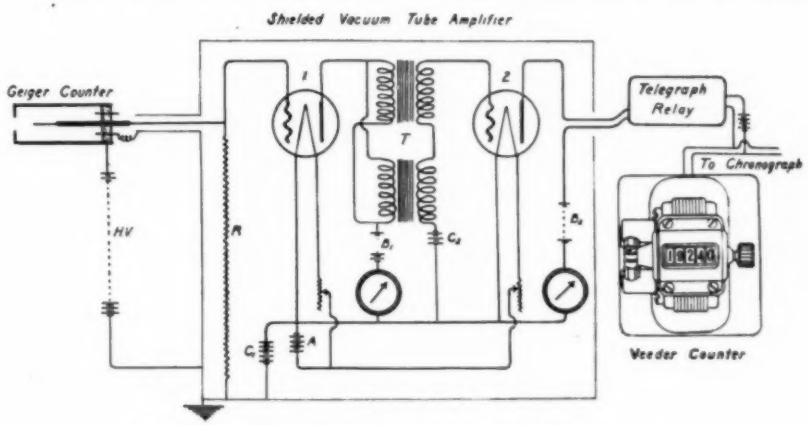


Fig. 1. Diagram of amplifier used with Geiger counter.

filled[4] tube, 2, in the second stage. The biasing battery, C_2, for this tube is adjusted so that the plate current is normally zero. By using a relatively high plate voltage a rush of current is secured when the grid potential is momentarily raised by the impulse communicated through the first stage by the counting chamber. This current ceases as soon as the grid potential falls to its normal value. The large momentary current in the second tube is mainly the result of ionization of the gas which the tube contains, as is evidenced by the glow accompanying each impulse. This arrangement gives the most satisfactory amplification of all the many tried in this laboratory for the purpose. With any of the usual types of radio tubes in the first

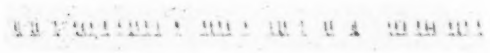
[3] H. Geiger, Zeits. f. Physik **27**, 7 (1924).

[4] This tube was kindly loaned by the Research Laboratory of the General Electric Company.

stage, and a similar gas-filled tube in the second, there is an instantaneous current of several milliamperes in the output circuit for each impulse. A further reason for the marked success of this arrangement is that the gas tube tends slightly to prolong the very brief impulse which is communicated to it. Therefore, the amplifier very easily operates an ordinary telegraph relay of about 1200 ohms resistance. This relay in turn actuates a Veeder electrical counter and chronograph pen as indicated in the figure.

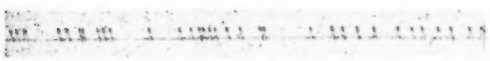
In an effort to learn why a steel needle treated with metaphosphoric acid should work, several points were prepared in this way. Best results were obtained by using cold concentrated acid, coating the point well with it, and wiping it thoroughly with cloth. About nine out of every ten points prepared in this way would count at once. Some typical records taken with these points are shown in Fig. 2. Line 1 is a record made with a freshly

No. 1. Freshly sharpened. 1300 volts.



No. 2. No. 1 dipped in phosphoric acid. 134/min. bl. 0. 1440 volts.

No. 3. Freshly sharpened. 1220 volts.



No. 4. Point No. 3 dipped in H_2SO_4. 124/min. bl. 0. 1320 volts.

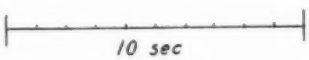


Fig. 2. Chronograph records showing behavior of steel points when treated with acid.

sharpened steel point. This record represents a more or less continuous succession of rapid discharges which set in as soon as the voltage is raised above a certain value, depending on the sharpness of the point and its distance from the walls of the chamber. If the voltage is raised a very little higher after this stage is reached a true arc strikes melting the needle point. Therefore this behavior, which is quite characteristic of a freshly sharpened metal point when it is the negative electrode, seems to be of the nature of an incipient arc. Nearly all freshly sharpened metal points behave in this way as soon as the voltage applied to the counting chamber is raised to the stage where a permanent discharge sets in. In this condition no noticeable effect can be produced on the discharge by allowing α-particles or β-particles to enter. Line 2 is a record which shows how the same point counts α-particles after being dipped in metaphosphoric acid and wiped. The portion of the

record shown represents about fifteen seconds, as can be seen from the time scale included in the figure. This point gave a natural effect or blank (i.e., with the source of α-particles removed) of zero when timed for one or two minutes.

Since metaphosphoric acid attacks steel, though slowly, it was first thought that the phosphate thus formed supplied the electrically resistant layer which enables these points to function. But steel points were coated with phosphate by other methods and failed to work. It was then observed that most of the steel points, when examined under a microscope, were still undergoing a slow attack from the film of acid left on them. Minute bubbles

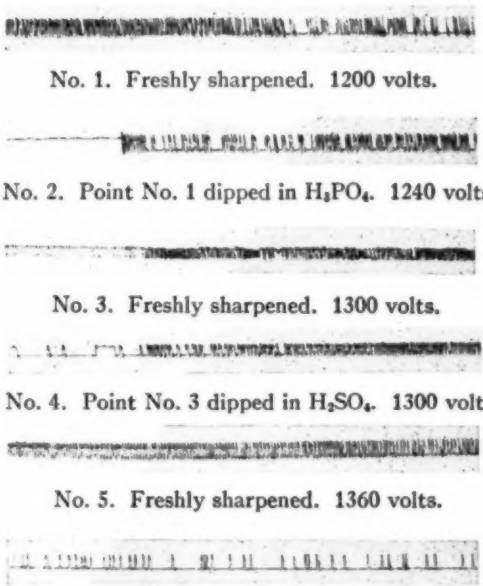

No. 1. Freshly sharpened. 1200 volts.
No. 2. Point No. 1 dipped in H_3PO_4. 1240 volts.
No. 3. Freshly sharpened. 1300 volts.
No. 4. Point No. 3 dipped in H_2SO_4. 1300 volts.
No. 5. Freshly sharpened. 1360 volts.
No. 6. No. 5 electrolyzed in H_2SO_4. 124/min. bl. 7. 1200 volts.
10 sec

Fig. 3. Chronograph records comparing the behavior of platinum points when treated by acids and when electrolyzed.

of hydrogen were still forming an hour or more after the point had been treated. This observation led to the following considerations and experiments.

If the hydrogen formed as a result of the chemical action was responsible for the action of the steel point, an obvious check was to dip the point in some other acid, as dilute sulphuric, which also attacks steel readily. This was tried with success. Fig. 2, line 3, shows a freshly sharpened steel point, and line 4 the same point counting α-particles after being dipped for a few seconds in sulphuric acid. Further, points made of metals not attacked by acids with which they were treated should show no effect. Some records

taken to test this view are shown in Fig. 3. Line 1 is the record of a freshly sharpened platinum point. Line 2 is a record obtained after dipping it in phosphoric acid, showing no improvement. A similar result is shown in lines 3 and 4 after dipping in sulphuric acid. A further check resulted from experiments with nickel and copper. Nickel is less readily attacked by the acid than steel and this is even more true of copper. Nickel would only work after prolonged treatment with cold acid and it was found necessary to warm the acid in the case of copper. As soon as the temperature was raised sufficiently to induce chemical action, the copper likewise became a good counting point. These experiments indicate strongly that it is the hydrogen formed by the chemical action and adhering in part at least to the point that enables it to count. If this is so, one might expect a layer of hydrogen applied by different means to work. Accordingly a platinum point was prepared by using it as an electrode in a dilute acid solution. The results of these experiments, shown in Fig. 3, lines 5 and 6, confirm the supposition that a layer of gas is responsible for the action of the point. After repeated trials it was found that it made little difference whether the platinum was used as anode or cathode in the electrolysis. We infer from this that a layer of gas is necessary but it may be either hydrogen or oxygen. Points prepared in this way usually do not retain their sensitive condition for more than a few hours, indicating that the layer is not held very firmly. It must also be borne in mind that a point working in air at atmospheric pressure presumably would not retain a heavy layer of hydrogen very long, so that most points owe their sensitivity to a layer of oxygen.

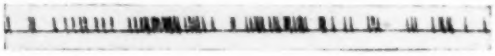
The foregoing experiments suggest that a layer of gas adhering to a metal point puts it in condition to count. In fact, from the evidence presented above, this layer seems necessary. However, it is also important to note that all treatments discussed so far will also produce *catalytic* surfaces. Recent investigations of this subject have brought forward the idea that such surfaces are very rough and have a loose and open metallic structure. This structure adsorbs gas very readily. The efficiency of the catalyst has been attributed to the existence of free metal ions in this surface layer. If it is true that the success of the previous methods is to be attributed to the catalytic nature of the surfaces and their consequent ability readily to acquire a layer of gas, good points should result from other surfaces which are catalytic. To test this idea points were prepared by coating platinum needles with platinum black by electrolysis in a platinum solution. They worked very successfully. Since the platinum black *surface* is all that is required on the views here presented, one would expect steel points coated with platinum black to work equally well, and this was found to be true. Since it is a very simple matter to coat steel needles with platinum black, merely by dipping them into a platinum solution, points were usually prepared in this way. This method of preparation always gives very satisfactory points, many of which last for several days. Some typical results with such points are shown in Fig. 4, lines 1 and 2. After standing for some time they often work as well as initially, and of course redipping a point for a few minutes

in the platinum solution also restores it. Since iron oxide is a catalyst for some reactions and has been used successfully also in point-counters, oxidized steel needles were also tried. By using great care not to carry the oxidation too far, very satisfactory results were obtained, as shown in lines 3 and 4 of Fig. 4. While not quite as sure a method as that using platinum black, the iron oxide points once prepared were most permanent, sometimes holding for weeks.

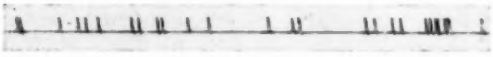
To make quite certain that it is the *catalytic* nature of the metallic surface with which we are dealing a series of experiments were undertaken at the suggestion of Dr. J. H. Hibben. In the first place a good test of the catalytic theory is provided by some metallic point which does not work in

No. 1. Freshly sharpened. 1350 volts.

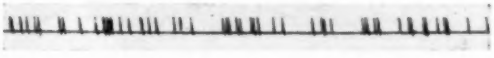
No. 2. Point No. 1 platinized. 80/min. bl. 1. 1420 volts.



No. 3. Freshly sharpened. 1330 volts.



No. 4. Point No. 3 oxidized in flame. 85/min. bl. 0. 1330 volts.



No. 5. Point No. 4 counting B-particles. 200/min. bl. 0. 1330 volts.

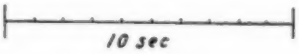


Fig. 4. Chronograph records of platinized and oxidized steel points.

the Geiger counter at all under ordinary treatment but which by special manipulation may be put into a catalytic condition. Copper is an example. All ordinary flame treatment of copper fails to produce a point which will work. However by repeated slow oxidation and reduction at about 250°C copper becomes a very good catalyst. Consequently points were prepared by this method and found to work very well.

A further test is provided by so-called catalytic "poisons." It is well known for example that mercury vapor, sulphur dioxide or hydrogen sulphide will ruin the activity of most metallic catalysts. It should therefore be interesting to admit these substances to the counting chamber while in operation. The results of some of these experiments are shown in Fig. 5. As soon as the poison in question is admitted to the chamber, as indicated

by the position of the arrow, the counter ceases to function *at once*. This is regarded as an extremely emphatic confirmation of the catalytic theory since all points which have been tried have responded in the way indicated by the records shown in Fig. 5.

In the light of these results there can be little question that points used previously by other investigators, however prepared, have depended for their sensitivity on a gas layer held to the surface by virtue of its catalytic nature. The exceptional behavior of some metals which fail to yield good points with the usual simple treatments is to be referred to the difficulty with which they can be put into a catalytic condition. In this connection the behavior of palladium is interesting. Its well-known affinity for hydrogen led the writer to try palladium points since one might expect a heavy adsorbed layer of hydrogen. However, glowing in a flame, electrolysis, or any other simple

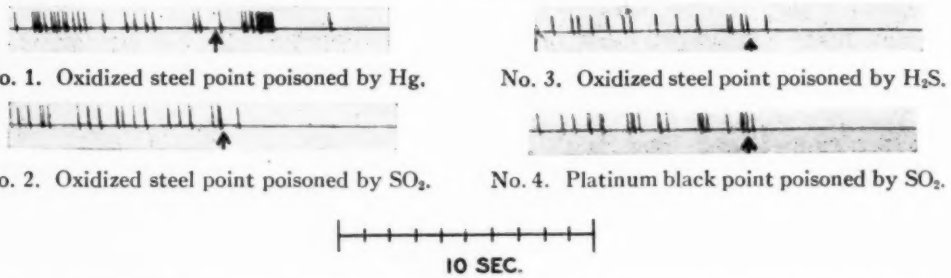

No. 1. Oxidized steel point poisoned by Hg.
No. 3. Oxidized steel point poisoned by H_2S.
No. 2. Oxidized steel point poisoned by SO_2.
No. 4. Platinum black point poisoned by SO_2.
10 SEC.

Fig. 5. Chronograph records showing that sensitive points are destroyed by catalytic "poisons."

treatment failed. One seems forced to the conclusion that it is not as easy to develop a catalytic surface on palladium as on platinum, for example. If the adsorbed gas exists, as presumably it does, it is in a different condition from that existing on a catalytic surface. This difference, in part at least, is to be attributed to the very loose structure of a catalytic surface which enables metallic ions to become a part of the adsorbed gas layer and in particular permits the free electrons of the metal to enter the gas layer more readily. This is substantiated by the observation that *palladium black*, a good catalyst, also makes a good surface for a point. The idea that the electrons from the metal form a part of the gas layer adsorbed on a catalytic surface is an important feature of one of the explanations of the action of the counter to be offered in this paper.

On the basis of the foregoing experiments, and other well established facts concerning the operation of these counters, the following discussion of the action of the counter is offered. In presenting these ideas it will be assumed at the outset that the sensitive area is on the point, in agreement with the experimental evidence presented above and with the experience of most other investigators. The anomalous results obtained by Kutzner are capable of an entirely different interpretation from that which he gives them, as will be shown. Furthermore the main discussion will be restricted to what may be termed the "normal" method of using the counter, i.e., with the chamber walls at a positive potential. All investigators agree that the counting chamber works most satisfactorily this way. However,

the views discussed here are equally applicable to the reversed potential as will be pointed out. Before going into more detail it is perhaps well to recall that under the conditions which a counter operates, i.e., high pressure and moderate voltage, only the electrons can acquire enough energy to ionize in the volume of the chamber. The positive ions never acquire kinetic energy greater than a few hundredths of a volt. This is a very important fact which must be considered in explaining the action of the counter, and which has been generally overlooked.

It seems desirable to present two alternative views of the sensitive area on the point both of which depend on a heavy layer of adsorbed gas on the surface of the point. One may be termed the "ionization" theory of the gas layer and the other the "evaporation" theory. On the ionization theory the action of the counter may be described in the following manner. The voltage on the chamber is raised to a point just below which a permanent discharge will set in. At this stage no electrons can be drawn from the point for all ions initially present in the counter have been swept out on applying the voltage, and there is no mechanism for releasing the electrons undoubtedly present in the layer of gas. If now an α or β-particle enters the chamber and produces a few ions, the positive ions are drawn down to the point. As mentioned above, since the counter works at atmospheric pressure or a considerable fraction of an atmosphere, there is no opportunity for the positive ions, as a result of their great mass and low mean free path, to acquire enough energy to ionize the gas in the chamber. It may now be recalled, however, that an adsorbed gas layer has a considerably lower ionization potential than the same gas in the free condition. This may be due to the fact that it exists there in an *excited* state. Kistiakowsky[5] has noted that nitrogen in the adsorbed condition has its ionization potential reduced by about five volts. He worked at fairly low gas pressures and it may be that at atmospheric pressure the gas layer assumes a condition in which it is even more readily ionized, although there is at present, I believe, no evidence for this. Nevertheless, as the positive ions approach the layer of gas they may be able to pull electrons from parent atoms in the layer by electrostatic attraction arising from their elementary positive charge. It would only be necessary for them to approach within a distance of the order of an atomic diameter to provide ionizing energy corresponding to several volts.* *Once a few electrons are thus released* it is relatively easy to account for the remainder of the process. These electrons are liberated in the very intense field existing near the point and as a result of the great mobility and comparatively large mean free path, they soon acquire energy enough to ionize the gas and the ionization current then builds up exponentially until the disturbance thus started has moved out of the strong electric field. It soon passes a region beyond which very little new ionization is produced. The positive ions, initially

[5] G. B. Kistiakowsky, Jour. Phys. Chem. **30**, 2356 (1926).

* *Note added in Proof.* Professor J. Franck has called my attention to the fact that under the conditions here postulated the *potential* energy of the positive ion also becomes available to help ionize the adsorbed gas layer as soon as the positive ion strikes it.

formed during this rush of current, move to the point and release additional electrons by ionizing the gas layer as the original ions did. This process can continue only so long as un-ionized gas atoms exist on the very tip of the point where the strong field is concentrated. Since it is reasonable to assume that these atoms remain ionized for a period perhaps of the order of 10^{-4} of a second before recombining by pulling electrons through the metal surface, there is a brief instant during which the returning positive ions can release no more electrons from the gas layer. Also, a layer of positive charge is formed on the tip of the point which reduces the field between the point and the chamber walls. These two process together then account for the automatic cessation of the current. To restore the counter so that it may respond to the next particle it is only necessary for the atoms of the gas layer to recombine at the expense of the abundance of free electrons in the metal of the point. If these processes may occur in about 10^{-3} of a second or less, as seems probable, they account for the action of the counter very readily.

At this stage of the work it occurred to the writer that, if such ionization existed in the gas layer, the recombination might produce a visible though faint flash for each particle counted. Accordingly a chamber was prepared for observation by cutting a narrow slot in one side opposite the point. A microscope with a magnifying power of about one hundred was carefully focussed on the very tip of the point. The amplifier was connected so that a click could be heard for each particle counted. The room was completely darkened. After allowing time for the eyes to adjust themselves, varying for different observers, a tiny flash could be seen on the tip of the point coincident with each click! Four different observers had an opportunity to view this action and all agreed that the clicks were simultaneous with the flashes within the limits of observation, and that there was complete coincidence between them. Furthermore this observed glow did not extend into the gas but appeared as a luminous cap on the tip of the magnified point.

The experiment described in the foregoing paragraph was regarded as a conclusive proof of the "ionization" theory when first observed. However, on second thought it was apparent that this glow on the point may be accounted for in a slightly different manner. The positive ions formed in the volume of the chamber have no opportunity to recombine until they reach the point since the intense field keeps this region swept clean of electrons. Consequently the recombination observed is certainly partly and may be wholly due to the recombination of these ions on their arrival at the point. On the assumption that they contribute the whole effect observed, the "evaporation" theory of the gas layer has been developed. In many respects it is more satisfactory than the ionization theory. Davisson and Germer[6] have shown in their experiments on reflecting electrons from a metal surface that an adsorbed gas layer begins by forming a lattice pattern on the surface. The character of this lattice pattern is determined by the crystal structure of the metal on which the gas adsorbs. They have further shown

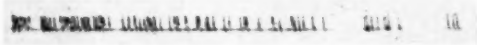
[6] Davisson and Germer, Phys. Rev. **30**, 705 (1927).

that adsorption of gas will continue at higher pressures until this simple structure of the layer has been destroyed. It is with such heavier layers of gas that we are dealing in the point counter. We may now assume that the sensitive condition of the point consists of such a heavy layer into which some of the free electrons of the metal have diffused. For with such a layer on the surface it may be that the sharp boundary conditions between metal and gas have been partially removed so that such ideas as "work function" and "image force" no longer apply as far as getting electrons into this gas layer. This assumption becomes even more reasonable when we recall that the metal surface is in a catalytic condition. We may now picture the process as follows. The positive ions formed by the α or β-particle on impinging on the point, drive off or "evaporate" the gas layer. The energy required to do this is much less than to ionize the gas, so it is easy to see how this may happen. As the gas layer is evaporated the excess electrons which have diffused into it are released and the remainder of the process occurs much as before. The rush of current ceases as soon as all the detachable gas molecules are driven off the point. The brief time required to readsorb a fresh layer provides the short lag necessary to interrupt the current. Since this readsorption will occur very readily with a catalytic or activated surface in gas at a considerable portion of an atmosphere pressure, the point quickly secures a fresh layer of gas into which the electrons diffuse and the chamber is ready to repeat. In fact, the positive ions which are drawn to the point, once they have recombined, automatically provide this adsorbed layer.

When the counter is operated with the potential reversed, the gas layer is less important and the operation may be regarded as follows: As the first electrons produced initially proceed to the point, they must approach within a few millimeters before they reach the intense field where they may quickly acquire sufficient energy to produce new ions. They then ionize the gas and the current builds up exponentially until the disturbance reaches the point. Since the positive ions produced in this process cannot ionize by impact, there is no way in which any part of the gas can contribute to this rush of current other than that between the place where the electrons first began to ionize as a result of energy acquired from the field and the point itself. Consequently the disturbance merely travels down to the point and must stop until a fresh supply of electrons are provided from the outer volume of the chamber. In this case any glow at the surface of the point must be due to an ionized gas layer on the surface. Observations on the glow, with the potential reversed, indicate that it is still there but much fainter. There does not seem to be such a sharp correlation between the flashes and the clicks of the relay, however. The fact that glow still persists seems to favor the ionization theory. On the view presented in this paragraph of the operation of the counter with the point positive, it should not matter what the nature of the metal surface of the point is. We have found this to be the case. Freshly sharpened metal points work at once when positive which would not work at all if negative. This fact seems to support the explanation

presented above. Furthermore we have found that the action of the chamber with the point positive is entirely independent of the presence of catalytic poisons.

Attention should be called to the fact that, although somewhat different processes are involved in the operation of the counter in the opposite directions, the major contribution to the current is obtained in the same way in each case from about the same region of the counter. That is, the great bulk of the current in both cases builds up exponentially in a fairly small volume of gas in the neighborhood of the point where the intense field exists. Consequently one would expect the counter to operate at about the same voltage in each case but be somewhat more difficult to control when the point is positive. This has been observed to be the case by Bothe,[7] who reports that the voltage is about the same in each case but that the working range of voltages is smaller for the positive point and the quantity of charge passing for each discharge somewhat less. This latter fact is to be anticipated from the above description since presumably a smaller volume



No. 1. Steel point, freshly sharpened. 1100 volts.

No. 2. Pt point, freshly sharpened. 200/min. bl. 63 1220 v.

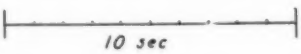


Fig. 6. Chronograph records of points showing recovery during operation.

of gas is active in this case. Furthermore, since, on the basis of the above consideration, the ionization current for each impulse will be produced in the same volume of gas at constant voltage and gas pressure, one would expect approximately the same quantity of electricity to pass for each impulse. Geiger[3] has made observations which show that this is true.

When the counter is working with the point negative one would expect a bad point to pick up a gas layer under the action of the discharge and begin to count properly; at least occasionally when conditions were just right. We have succeeded in obtaining records of this kind in the case of steel and platinum, as shown in Fig. 6. Both give initially a very rapid series of pulses but soon quiet down and count normally, although such points never become fully reliable. It is undoubtedly something of this kind that accounts for the action of an ordinary discharge tube at much lower gas pressures. In such a case one is also confronted with the difficulty of getting electrons from the cold cathode.

[7] W. Bothe, Zeits. f. Physik **37**, 552 (1926).

It is now of some interest to return to the work of Kutzner[2] which led him to suppose that the sensitive layer was on the inside face of the chamber. He bases his conclusion principally on the observation that an α-particle in his experiments must pass through a region very close to the face or it is not counted. The explanation for this curious condition is as follows: In the case of a sharp point, as Kutzner used, the volume through which an α-particle must pass to be counted is of the form indicated in Fig. 7(b) as experiments in this laboratory have shown. The sharper the point the more constricted this volume becomes, particularly in the neighborhood of the point. Hence, the chance that an α-particle will traverse this active region when shot towards it at right angles is very slight; and, even if it went through it, enough positive ions might not be produced to start the counter off. However, if particles are shot through the volume near the face, even at right angles to the axis of the chamber, counts are readily obtained as we have repeatedly observed. Kutzner's negative result even under these conditions appears to be caused by the aluminum foil used to cover the slot in his chamber. The path which an α-particle must traverse in the foil when shot in at this angle would be relatively large so that under these conditions the stopping power of the foil would exceed the range of the α-particle. If a ball point is used the active volume has the form indicated in Fig. 7(a), and under proper conditions counts can be obtained fairly close to the point. All that these active volumes mean is that ions produced outside them never reach the sensitive part of the point, nor the region of intense fields, as a result of the shape of the electrostatic field. Therefore, Kutzner's results do not indicate that the sensitive area is on the inner side of the face but rather conclusively prove it to be on the point.

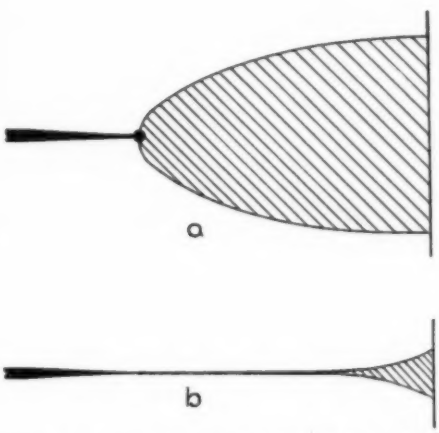


Fig. 7. Diagrams showing the volume through which an α-particle must pass to be registered by the Geiger counter. (a) Ball point. (b) Sharp needle point.

In conclusion I should like to thank Mr. H. L. Martin who helped build the apparatus and assisted in the observations. I am also indebted to the Kelly Hospital of Baltimore for the old radon tubes from which the sources were extracted.

BUREAU OF STANDARDS,
WASHINGTON, D. C.,
February 15, 1928.

THE DIFFUSION PROBLEM FOR A SOLID IN CONTACT WITH A STIRRED LIQUID

By H. W. March and Warren Weaver

Abstract

A cylindrical solid of length a in a direction x and arbitrary cross section normal to x is in contact on its plane face $x=a$ with a well stirred liquid. The face $x=0$ of the solid and the lateral surface are impervious to heat. The liquid extends from $x=a$ to $x=a+b$, there being no loss of heat across the face $x=a+b$. The initial temperature of the solid and liquid being given, a Volterra integral equation of the second kind with discontinuous kernel is obtained for the temperature of the liquid as a function of the time. The solution of this integral equation is obtained in terms of the roots of a transcendental equation and the roots of an infinite system of linear equations. By means of the theory of singular integral equations, it is shown that the differential equation and boundary conditions possess but one solution of required type, which solution is obtained from the integral equation. The connection of this problem with a case of material diffusion is shown, and a numerical illustration is given. The theory suggests a new method of determining directly and accurately the thermal conductivity of solids.

1. Statement of the Problem.

THE problem here considered is that of the one-dimensional flow of heat which occurs when a solid, of length a in a direction x, is in contact, on the plane face $x=a$, with a well stirred liquid, the other face $x=0$ being impervious to heat. In order that the flow of heat be one dimensional, it is necessary, as in all similar problems, either that the solid and the liquid be each infinite in extent in directions normal to x, or that they be cylindrical bodies of the same cross-section whose lateral surfaces are impervious to heat. Let the liquid extend from $x=a$ to $x=a+b$, there being no loss of heat, by radiation or conduction, across the face $x=a+b$. Let $u(x,t)$ represent the temperature in the solid at any point x and time t, and let $v(t)$ represent the temperature of the liquid at any time t. The function $v(t)$ must be continuous for all values of t. Then

$$\alpha^2\partial^2u/\partial x^2=\partial u/\partial t, \quad t>0, \tag{1}$$

where α^2, the diffusivity of the solid, is the quotient of its thermal conductivity k by the product of its density ρ and specific heat c.
Also,

$$\partial u/\partial x=0, \quad x=0, \quad t>0, \tag{2}$$

and

$$\lim_{t=0} u(x,t)=u_0(x), \quad 0\leqq x\leqq a, \tag{3}$$

where $u_0(x)$ is the initial temperature of the solid. The thermal contact of the solid and the liquid at $x=a$ gives the condition,

$$u(a,t)=v(t), \quad t>0. \tag{4}$$

If the initial temperature of the liquid be v_0, then its temperature at time t is given by

$$v(t) = v_0 - \frac{k}{K}\int_0^t \left(\frac{\partial u}{\partial x}\right)_{x=a} dt,$$

where K is the heat capacity of a prism of the liquid of unit cross section and length b. From this equation one obtains, by differentiation, the condition

$$K\partial v/\partial t = -k(\partial u/\partial x)_{x=a}. \tag{5}$$

The question of the existence and uniqueness of the solution of Eqs. (1) to (5) will be considered in Section 3.

In an experiment in colloidal chemistry, a mass M of a material is uniformly distributed, at time zero, in a jelly of depth a. This jelly is covered with a depth b of water which is kept stirred. The material diffuses through the jelly and into the water, where its concentration is determined as a function of time by analyzing samples. It is desired to determine the coefficient of diffusion of this material in the jelly from the experimental time—concentration curve of the liquid. If one assumes this problem to be entirely analogous to the thermal problem stated above, the solution of the concentration—diffusion problem can be obtained at once from the solution of the heat problem. For by comparison of the fundamental thermal equation

$$\Delta(\text{temperature}) = \Delta(\text{heat})/c\rho V,$$

where ρ is density, V volume, and c specific heat; and the equation

$$\Delta(\text{concentration}) = \Delta(\text{mass})/V$$

it is seen that one need only replace ρc by 1 to pass from one problem to the other. *Thus when u and v are interpreted to mean concentrations, α^2 is to be replaced by k, and K is to be replaced by b.*

It is not proposed to discuss here the legitimacy of the identification of the two problems. It is, however, clear that Eq. (4) is the doubtful one. If it is found that, when a steady state has been finally reached, the concentration of the diffusing material is the same in the jelly and in the liquid, then this experimental fact furnishes reasonably convincing evidence for this assumption. For it indicates that there is indeed equilibrium when the concentrations are equal in the liquid and in the jelly; and sufficiently thin layers of the jelly and liquid, adjacent to the plane of contact, may be assumed to be in continuous equilibrium as the diffusion proceeds. Actual stirring of the liquid cannot, of course, assure at all moments a uniform concentration in the liquid down to the surface of the jelly, but the diffusion proceeds slowly, in an actual case, so that the assumed conditions are closely approximated.

In explanation of the method of solution which occurs in the next section, it may be remarked that the characteristic functions of (1) under the

conditions (2) and (5) are not orthogonal; so that the usual method meets a difficulty in attempting to satisfy (3). It should also be noted that Eqs. (1), (2), (3), (4), and (5) are satisfied, for the special case $u_0(x)=u_0$, a constant, by the values $u=u_0$, $v=u_0$. If $u_0 \neq v_0$, it is obvious that the values just written do not furnish a solution of the physical problem. The mathematical condition which is not met, is the condition that $v(t)$ be a continuous function for all values of t including $t=0$. The method of solution must proceed in such a way as to safeguard this required continuity of $v(t)$.

2. Solution of the Problem.

In this section a solution of Eqs. (1) to (5) inclusive will be obtained, neglecting for the moment certain questions of rigor. These questions will be raised and answered in the succeeding section.

Let

$$u=u_1+u_2,$$

where u_1 and u_2 satisfy (1) and the conditions

$$\partial u_1/\partial x=0,\ x=0:\ u_1(a,t)=0,\ t>0\ ;\ \lim_{t=0} u_1(x,t)=u_0(x). \tag{7}$$

$$\partial u_2/\partial x=0,\ x=0:\ u_2(a,t)=v(t),\ t>0:\ \lim_{t=0} u_2(x,t)=0. \tag{8}$$

The function u_1 is given by the known formula

$$u_1=\sum_{n=0}^{\infty} A_n e^{-\alpha_n t}\cos \mu_n x \tag{9}$$

where $$\alpha_n=\alpha^2\mu_n^2\ ;\ \mu_n=(2n+1)\pi/2a\ ;\ A_n=2a^{-1}\int_0^a u_0(x)\cos\mu_n x dx. \tag{10}$$

The Fourier expansion here used which involves only odd multiples of $\pi/2a$ can be readily obtained by writing an ordinary cosine expansion in the interval from $x=0$ to $x=2a$ of a function $u(x)$ defined by $u(x)=u_0(x)$, $0\leqq x\leqq a$; $u(x)=-u_0(2a-x)$, $a\leqq x\leqq 2a$.

If, in particular, $u_0(x)$ be a constant, say u_0, then

$$A_n=\frac{4}{\pi}\frac{(-1)^n}{2n+1}u_0. \tag{11}$$

Now let $H(x,t)$ be the temperature which the solid would have, at a point x and time t, if it were initially at zero temperature, if its face $x=a$ were maintained at temperature unity, and if its face $x=0$ were impervious to heat. It is easily seen that the function

$$H(x,t)=1-\frac{4}{\pi}\sum\frac{(-1)^n}{2n+1}e^{-\alpha_n t}\cos\mu_n x \tag{12}$$

satisfies these requirements. The function u_2 is now given, in terms of $H(x,t)$ by Duhamel's theorem,[1] as

$$u_2 = \int_0^t v(\tau)\frac{\partial}{\partial t}H(x,t-\tau)d\tau = -\int_0^t v(\tau)\frac{\partial}{\partial \tau}H(x,t-\tau)d\tau,$$
$$= v_0 H(x,t) + \int_0^t \left(\frac{\partial v}{\partial \tau}\right) H(x,t-\tau)d\tau. \tag{13}$$

Let the expressions for u_1 and u_2 be added to form u, and the value of $H(x,t)$ be inserted from (12). It then follows that

$$\left(\frac{\partial u}{\partial x}\right)_{x=a} = -\frac{K}{k}\sum_0^\infty C_n e^{-\alpha_n t} + \frac{2}{a}\int_0^t \frac{\partial v}{\partial \tau}\sum_0^\infty e^{-\alpha_n(t-\tau)}d\tau, \tag{14}$$

where $$C_n = \kappa\left[\tfrac{1}{4}A_n(-1)^n(2n+1)\pi - v_0\right], \quad \kappa = 2k/aK. \tag{15}$$

In obtaining (14) it has been assumed legitimate to perform the differentiation with respect to x under the sign of integration and the sign of summation. This point will be later considered. In case $u_0(x) = u_0$, a constant, Eq. (15) reduces to the special form

$$C_n = \kappa(u_0 - v_0). \tag{15'}$$

If, now, (14) be substituted in (5) the result is

$$F(t) = f(t) - \int_0^t F(\tau)K(t-\tau)d\tau, \tag{15}$$

where $$f(t) = \sum C_n e^{-\alpha_n t}; \qquad K(t) = \kappa\sum e^{-\alpha_n t}; \qquad F(t) = \partial v/\partial t. \tag{17}$$

Unless otherwise stated, sums such as (17) are to be understood throughout the paper to extend from $n=0$ to $n=\infty$.

The Volterra integral Eq. (16) can be solved by an immediate extension of the method developed by Whittaker[2] for the numerical solution of an equation whose kernel is expressed as a finite sum of exponentials. If, in fact, one substitutes in (16) the assumption

$$F(t) = \sum B_i e^{-\beta_i t} \tag{18}$$

the resulting equation will be satisfied if the coefficients of $e^{-\beta_i t}$ and of $e^{-\alpha_n t}$ are, for all i and n, the same on the two sides of the equation. Of the two conditions so obtained, the first demands that each β_i satisfy the equation

$$1 + \sum_{n=0}^{\infty} \frac{\kappa}{\alpha_n - \beta_i} = 0. \tag{19}$$

That is, the numbers β_i are the roots of the transcendental equation

$$1 + \sum \frac{\kappa}{\alpha_n - y} = 0. \tag{20}$$

[1] Carslaw, The Conduction of Heat, 1921, p. 17.

[2] E. T. Whittaker, On the Numerical Solution of Integral Equations. Proc. Royal Soc. London **94A**, 367–383 (1917).

The formula

$$\tan z=\frac{2z}{(\pi/2)^2-z^2}+\frac{2z}{(3\pi/2)^2-z^2}+\frac{2z}{(5\pi/2)^2-z^2}+\cdots$$

permits (20) to be rewritten as

$$\tan z+\lambda z=0. \tag{21}$$

where

$$y=\alpha^2z^2/a^2, \quad \lambda=\alpha^2K/ak=K/a\rho c. \tag{22}$$

It may be noted that λ is the ratio of the heat capacity of the liquid to that of the solid per unit area normal to x.

In the case of the material-diffusion problem, Eqs. (22) are to be replaced by

$$y=kz^2/a^2, \quad \lambda=b/a. \tag{22'}$$

The second condition, referred to above, demands that

$$C_n+\kappa\sum_{i=0}^{\infty}\frac{B_i}{\alpha_n-\beta_i}=0, \quad n=0,1,2,\cdots. \tag{23}$$

Thus (18) is a solution of (16) if the constants β_i are determined from (21) and (22) and the constants B_i then determined from (23).

Eq. (21) is a generalization of the equation

$$\tan z=z \tag{24}$$

met in many problems of applied mathematics. The method used by Lord Rayleigh[3] to obtain the roots of Eq. (24) can be applied to the more general Eq. (21). There results, as a formula for the n'th positive root (which is numerically equal to the n'th negative root) the equation

$$Z_n=W_n+w_n \tag{25}$$

where

$$W_n=\tfrac{1}{2}(2n+1)\pi \tag{25'}$$

and

$$w_n=\frac{1}{\lambda W_n}-\frac{3\lambda+1}{3\lambda^3W_n^3}+\frac{30\lambda^2+20\lambda+3}{15\lambda^5W_n^5}-\frac{1575\lambda^3+1575\lambda^2+483\lambda+45}{315\lambda^7W_n^7}$$
$$+\frac{39{,}690\lambda^4+52{,}920\lambda^3+24{,}696\lambda^2+3{,}834\lambda+9}{2835\lambda^9W_n^9}-\cdots \tag{25''}$$

In Fig. 1 the first four roots, z_0, z_1, z_2, z_3, of Eq. (21) are shown, for values of λ between 1 and 5. The roots beyond the fourth for these values of λ, and any roots for higher values of λ, may be calculated very easily from the equations (25). For smaller values of λ the formula converges very slowly, and the roots can be found more easily by a combination of a graphical and trial and error method. The discussion of this paper will be limited to the case $\lambda\geqq 1$.

[3] Rayleigh, Theory of Sound. 1896. Vol. I, p. 334.

Eqs. (23), from which the numbers B_i are to be determined, form an infinite system of linear equations. In Section 3 it will be shown that this system possesses a unique bounded solution, and in Section 4 a convenient method is given for the actual computation of the numbers B_i.

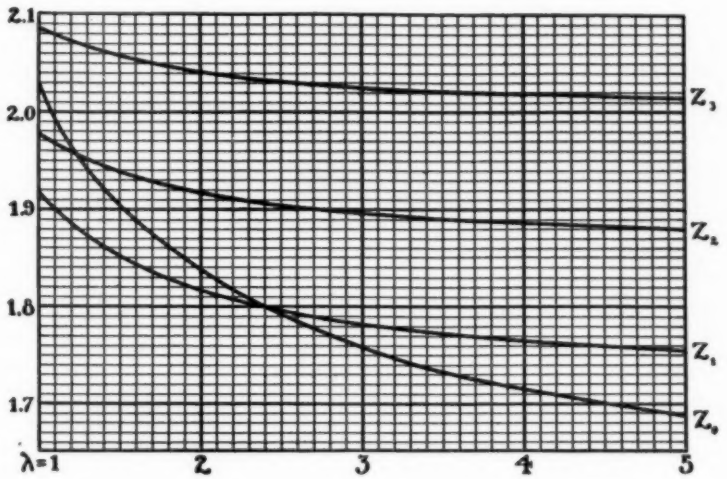


Fig. 1. This figure gives the first four roots, z_0, z_1, z_2, z_3, of the equation $\tan z+\lambda z=0$, for values of λ ranging from 1 to 5. For the curve z_0 the vertical scale reads as shown. For z_1, the values read from the curve should be increased by 3: for z_2, add 6: for z_3, add 9.

From (18) and (17)

$$\partial v/\partial t = \sum B_i e^{-\beta_i t}, \tag{26}$$

so that

$$v = D_0 - \sum (B_i/\beta_i) e^{-\beta_i t}.$$

Now the total heat which a cylinder of the solid of unit cross section will have lost in cooling from its initial temperature $u_0(x)$ to a final uniform steady temperature u_∞ is

$$\rho c a(\bar{u}-u_\infty), \text{ where } \bar{u} = a^{-1}\int_0^a u_0(x)dx.$$

The total heat which a similar cylinder of the liquid will have gained is $K(v_\infty - v_0)$, where, moreover, $v_\infty = u_\infty$. Thus $v_\infty = D_0 = (\bar{u}+\lambda v_0)/(1+\lambda)$.

Consequently

$$v = \frac{\bar{u}+\lambda v_0}{1+\lambda} - \sum \frac{B_i}{\beta_i} e^{-\beta_i t}. \tag{27}$$

For $t=0$, this equation reads, after reduction,

$$\sum (B_i/\beta_i) = (u-v_0)/(1+\lambda). \tag{28}$$

It must be possible to establish this surprisingly simple value for the sum of the quotients of B_i by β_i directly from Eqs. (19) and (23). Apart from its intrinsic interest, Eq. (28) furnishes a very convenient and convincing check on computed values of B_i and β_i.

If (26) be now substituted in (13), the resulting value of $u=u_1+u_2$ is given by

$$u=u_1+v_0H+\int_0^t \sum_{i=0}^{\infty} B_i e^{-\beta_i\tau}\left[1-\frac{4}{\pi}\sum_{n=0}^{\infty}\frac{(-1)^n}{2n+1}e^{-\alpha_n(t-\tau)}\cos\mu_n x\right]d\tau.$$

The term obtained, from the integral, when the factor 1 of the square bracket is used, is $v-v_0$. The remaining portion of the integral may be written

$$-\frac{4}{\pi}\sum_{n=0}^{\infty}\frac{(-1)^n}{2n+1}e^{-\alpha_n t}\cos\mu_n x\sum_{i=0}^{\infty}B_i\int_0^t e^{(\alpha_n-\beta_i)\tau}d\tau$$

$$=-\frac{4}{\pi}\sum_{n=0}^{\infty}\frac{(-1)^n}{2n+1}\cos\mu_n x\sum_{i=0}^{\infty}\frac{B_i e^{-\beta_i t}}{\alpha_n-\beta_i}+\frac{4}{\pi}\sum_{n=0}^{\infty}\frac{(-1)^n}{2n+1}\cos\mu_n x e^{-\alpha_n t}\sum_{i=0}^{\infty}\frac{B_i}{\alpha_n-\beta_i}$$

The second of these last written two terms may be simplified. In fact, using (23) and (17), this second term may be rewritten as

$$-\sum_{n=0}^{\infty}A_n\cos\mu_n x e^{-\alpha_n t}+\frac{4v_0}{\pi}\sum_{n=0}^{\infty}\frac{(-1)^n}{2n+1}\cos\mu_n x e^{-\alpha_n t}=-u_1-v_0[H(x,t)-1].$$

Thus,

$$u=v-\frac{4}{\pi}\sum_{n=0}^{\infty}\frac{(-1)^n}{2n+1}\cos\mu_n x\sum_{i=0}^{\infty}\frac{B_i e^{-\beta_i t}}{\alpha_n-\beta_i}. \tag{29}$$

In many problems of applied mathematics, the solution is expressed as an infinite sum of terms each of which satisfies the differential equation but not the boundary conditions. In the Ritz[4] metnod, the solution appears as a sum of terms each of which satisfies the boundary conditions but not the differential equation. It is interesting to note that u is here expressed as a sum of functions none of which separately satisfies either the differential equation or the boundary conditions. It may be checked, without difficulty, that the function u and v given by (29) and (27) do, by virtue of (19) and (23), satisfy all the conditions (1) to (5).

3. Analytical Details.

(A) *Existence and uniqueness.* It will now be shown that there exists one and only one solution $u(x,t)$ and $v(t)$ of conditons (1) to (5) for which v is a continuous function of t and for which u and $\partial u/\partial x$ are continuous functions of x and t in a region $0\leqq x\leqq a$, $0<\eta\leqq t\leqq T$, where η is an arbitrarily small quantity, and T is as large as one pleases.

We will refer to Eqs. (1) to (5) as Conditions I, and to Eqs. (1), (2), (3), (16) and equation

$$k(\partial u/\partial x)_{x=a}=-KF(t), \quad t>0 \tag{30}$$

as Conditions II. It will be shown that Conditions II permit one and only one solution of the required type, and that any solution of Conditions I is also a solution of Conditions II.

[4] W. Ritz, Gesammelte Werke, p. 251.

Since $\partial u/\partial x$ is to be a continuous function of t, so, also, by (30), is $F(t)$. The kernel $K(t-\tau)$ of the integral Eq. (16) is not continuous for $t=\tau$. It may be readily seen, however, that this equation comes under the theory developed by Evans;[5] thus (16) permits one and only one continuous solution $F(t)$, $0<\eta\leqq t\leqq T$. The function $F(t)$ being uniquely determined by (16), conditions (1), (2), (3), (30) are then a usual set of conditions for a thermal problem, and are known to permit one and only one solution $u(x,t)$.

It remains to show that a solution of I is necessarily a solution of II. That is, it is necessary to show that (16) follows from conditions I. Now if there is any function $F(t)=\partial v/\partial t$, then u is expressible uniquely in terms of $\partial v/\partial\tau$ and v_0 by means of Eqs. (1) to (4) as $u=u_1+u_2$, where u_1 is given by (9) and u_2 by (13). Eq. (16) follows from this formula and from (5) if it is permissible, in forming $\partial u/\partial x$, to differentiate u_1 under the sign of summation, and u_2 under the sign of integration and summation. Since the discussion is restricted to the range $0<\eta\leqq t\leqq T$, this question can be answered affirmatively at once for u_1, and also for the first term of u_2. It is thus only necessary to justify the equation

$$\frac{\partial}{\partial x}\int_0^t \frac{\partial v}{\partial\tau}H(x,t-\tau)d\tau=\frac{2}{a}\int_0^t\frac{\partial v}{\partial\tau}\sum_0^\infty(-1)^{n+1}e^{-\alpha_n(t-\tau)}\sin\mu_n x d\tau. \quad (31)$$

That this equation holds can be shown without difficulty.[6]

(B) *Existence and uniqueness of the roots of the infinite system of equations* (23). To investigate the convergence of the infinite system of Eqs. (23), from which the coefficients B_i are to be calculated, it is convenient to rewrite this system in the form

$$\sum b_{ni}D_i\equiv\sum_{i=0}^\infty\frac{m_n-(2n+1)^2}{m_i-(2n+1)^2}D_i=[m_n-(2n+1)^2]C_n\equiv C_n', \quad (32)$$

where
$$D_i=4a^2\kappa B_i/\pi^2\alpha^2,\quad m_i=4a^2\beta_i/\pi^2\alpha^2=4z_i^2/\pi^2. \quad (33)$$

The system (32) possesses, according to a theorem by von Koch[7] a unique bounded solution for the D_i provided that, for all n,

$$|C_n'|<C, \quad (34)$$

$$\sum_{i=0}^{\infty}{}'|b_{ni}|<1, \quad (35)$$

where C is a positive constant, and where the prime on the summation sign indicates that the term $i=n$ is to be omitted.

It may be shown without difficulty that these conditions are satisfied by the quantities b_{ni} and C_n' defined by (32).

(C) *Convergence of double series.* In obtaining (29) and in showing that the differential Eq. (1) and the boundary conditions (3) and (5) are satisfied, certain double series were rearranged. Due to the theorem referred to in

[5] G. C. Evans, The Integral Equation of Volterra of the Second Kind with Discontinuous Kernel. Trans. Amer. Math. Soc. **11** (1910), 393–413.

[6] Carslaw, Fourier Series and Integrals (1921), p. 156.

[7] V. Koch, Jahresbericht d. Deut. Math. Ver. **22**, 289 (1913).

section 3 (A), it is only necessary to investigate the absolute convergence of the series for $0<\eta\leqq t$ and $\tau<t$. Under these simplifying restrictions, the absolute convergence may be readily established.

4. Numerical Example.

To illustrate the computations involved, the solution will now be obtained for the case of diffusion of material, initially uniformily distributed with a concentration which will be called unity, from a solid of length a into a liquid region, initially free of the diffusing material, of the same length a. Then

$$u_0(x)=1,\ v_0=0,\ K=b=a,\ C_n=2k/a^2.$$

For $\lambda=1$ the first eight roots of Eq. (21) are,

$$z_0=\ 2.0288,\ z_1=\ 4.9132,\ z_2=\ 7.9787,\ z_3=11.0855$$
$$z_4=14.1775,\ z_5=17.3364,\ z_6=20.4692,\ z_7=23.6034.$$

These values are, by (22′) to be squared and multiplied by k/a^2 to produce the values β_i. Now Eqs. (23) for the determination of B_i may be written, since the constants C_n do not depend on n, in the form

$$\sum_{i=0}^{\infty}\frac{m_n-(2n+1)^2}{m_i-(2n+1)^2}\,B_i'=[m_n-(2n+1)^2],\tag{36}$$

where

$$B_i'=4a^2B_i/\pi^2k\tag{37}$$

The actual computation of the numbers B_i' is simplified by the observation that as i increases the constants B_i' all approach the value which the right-hand member of (36) approaches as n increases, namely, $8/\lambda\pi^2$; or, in this example, $8/\pi^2$. In fact, the coefficient of B_n' in the n'th equation is unity, while the coefficients off the principal diagonal become more nearly skew symmetric as n increases. Moreover, the coefficients rapidly decrease in absolute value as one goes from the principal diagonal. The value of the left member therefore arises almost entirely from the principal diagonal term, the other terms almost cancelling, pair by pair, and being, moreover, very much smaller even if they did not sensibly cancel. The evalution of the numbers B_i' was thus accomplished by tentatively assuming that all B_i' $i>3$, were sensibly equal to $8/\pi^2$. The first four equations (36) were then written

$$\sum_{i=0}^{3}\frac{m_n-(2n+1)^2}{m_i-(2n+1)^2}B_i'=[m_n-(2n+1)^2]-\frac{8}{\pi^2}\sum_{i=4}^{\infty}\frac{m_n-(2n+1)^2}{m_i-(2n+1)^2}\cdot\tag{38}$$

The value of the sum on the right can be readily computed to any desired degree of accuracy by summing, term by term, until the ratio of

$$1/[m_i-(2n+1)^2]\text{ and }1/m_i$$

is as nearly unity as is desired, and then noting that, for large i, we have $m_i\doteq(2i+1)^2$.

If the B_i', $i>3$, all differ from $8/\pi^2$ by less than an amount δ, the difference between the value of the last member of (38) when computed as just suggested, and its true value is less, in the case of the first equation, than

$$\frac{8\delta}{\pi^2}[m_n-(2n+1)^2]\sum_{i=1}^{\infty}\frac{1}{(2i+1)^2-(2n+1)^2}=0.036\delta.$$

The values of the first four roots B' as actually calculated from (38) are 0.545, 0.748, 0.789, 0.799. The last of these differs from $8/\pi^2$ by $\delta=.012$. The assumed right member of the first Eq. (38) thus differs from its correct value by less than (0.036) (.012) = 0.0004. Since the right member is approximately 0.668 a correction of the order just computed would have no effect on the significant figures retained.

The first four roots of Eqs. (36) were computed, in this way, for values of λ ranging from $\lambda=1$ to $\lambda=5$. These values are shown in Fig. 2. In order

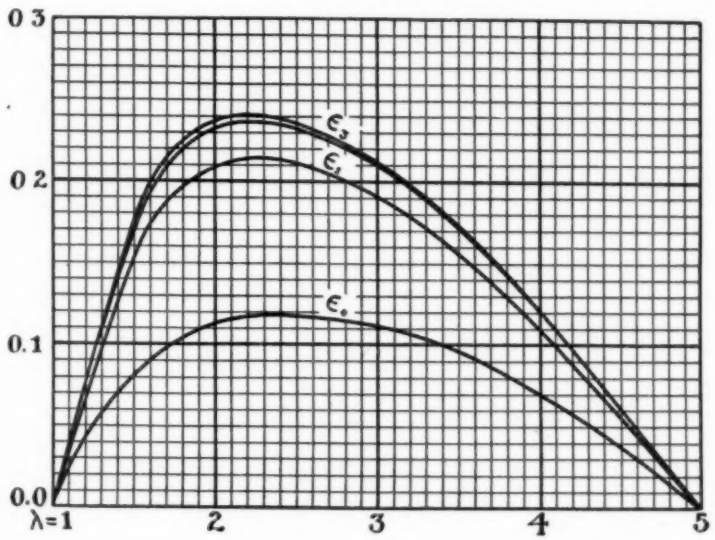


Fig. 2. From the values of ϵ_i given on this figure, the values of B_i' (see equation 36) can be computed from the formulas:

$$B_0'=-0.099\lambda+0.644-\epsilon_0$$
$$B_1'=-0.146\lambda+0.894-\epsilon_1$$
$$B_2'=-0.157\lambda+0.946-\epsilon_2$$
$$B_3'=-0.159\lambda+0.958-\epsilon_3$$

The values of B_i', where $i>3$ can all be computed from the formula,

$$B_i'=-0.162\lambda+0.972-\epsilon_3$$

to represent these values more accurately on a figure of reasonable dimensions, the values of B_i' are not shown directly, but rather the amounts ϵ_i by which the values of B_i' differ from a linear dependence on λ.

Eq. (28) may now be used to check these computed values of β_i and B_i. In fact, for the special case under consideration, (28) demands that

$$\sum(\pi^2B_i'/4z_i^2)=\tfrac{1}{2}.$$

If one uses the values of z_i and B_i' given above, for $i<4$, and, for $i>4$, the values $4z_i^2/\pi^2=(2i+1)^2$, $B_i'=8/\pi^2$, the left member will be found to check the right member to the fourth decimal place.

Eq. (27), for the concentration in the liquid, now reads

$$v=\tfrac{1}{2}-[0.327e^{-4.117T}+0.0766e^{-24.14T}+0.0306e^{-63.68T}+0.0160e^{-123T}+\cdots], \quad (39)$$

where $T=kt/a^2$.

The diffusion problem, namely, to determine the coefficient of diffusion k from the experimental time-concentration curve for the liquid, is now easily solved. The coefficient k fortunately enters Eq. (46) only as a multiplier of t.[8] Thus, if (39) be plotted and the values of T and t be observed corresponding to the same value v on the graph of (36) and on the experimental curve respectively, then $k=a^2T/t$.

In Fig. 3 is shown a graph of (39). The circles are values observed in the diffusion of urea from a gel into a layer of water. The experimental research from which these data were taken will be published elsewhere. The points are included here only to show that the theoretical result obtained is in close agreement with the facts.

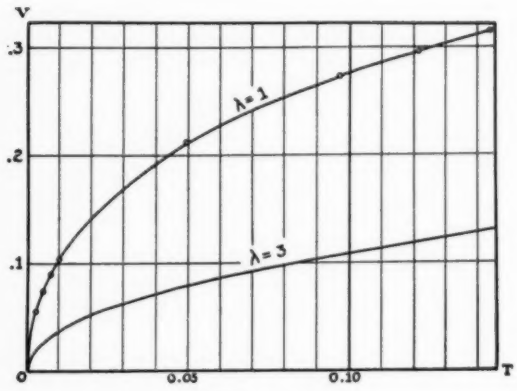


Fig. 3.

The particularly simple determination of the coefficient of diffusion from the concentration-time curve for the liquid suggests that a convenient method of determining coefficients of thermal diffusion could be based on such a method. The required data, namely, the temperature of the stirred liquid as a function of time, could be obtained much more easily than is the case with the data for many methods for such determinations. The boundary conditions on the face $x=a$ could, moreover, be met with a high degree of accuracy, the thermal convection in the liquid aiding materially in the stirring process in the layer of the liquid next to the solid.

DEPARTMENT OF MATHEMATICS,
UNIVERSITY OF WISCONSIN,
April 1, 1928.

[8] That this would be the case is obvious from equations (1) and (5).

ABSORPTION OF ULTRASONIC WAVES BY VARIOUS GASES

By T. P. Abello

Abstract

Absorption coefficient for ultrasonic waves in CO_2, N_2, H_2 and He.—A beam of ultrasonic waves with a frequency of 612 kilocycles from an oscillating quartz crystal was passed through a mixture of gas and air, contained in a brass absorption tube with ends covered by thin celluloid films. The design of the tube greatly reduced the effect of resonance and allowed the use of two different lengths of absorbing gas, leaving the geometrical arrangement of openings and absorbing screens the same. The emergent beam was allowed to fall upon another quartz crystal which had a natural frequency very nearly equal to the frequency of the waves and which was connected to the grid of a triode. The intensity of the received signal was measured by a previously calibrated vacuum tube voltmeter. A logarithmic decrease in the transmitted energy with increase in the percentage of the gas in the mixture was found with CO_2, N_2O, H_2, and He. The increase in the absorption coefficient (cm^{-1}) at 612 kilocycles when air was replaced by a mixture containing 1 percent by volume of the gas was found for CO_2 to be 0.029; for N_2O, 0.034, for H_2, 0.014, for He, 0.0025. For argon mixtures no absorption was observed.

Reflection of ultrasonic wave by a thin celluloid film. The fractional part of the beam which was transmitted by the films at the ends of the absorption tube, increased with increase in percentage of CO_2 and N_2O but decreased with increase in percentage of H_2 and He, agreeing qualitatively with Rayleigh's theory.

Introduction

IN THE course of his measurement of the velocity of ultrasonic waves in carbon dioxide, Pierce[1] noticed that at a frequency of 1,034 kilocycles the gas was practically opaque to the waves. Even at 98 kilocycles he noticed a much greater absorption in carbon dioxide than in air. The writer has observed the decrease of the transmitted intensity with increasing percentage of the gas for 612 kilocycle waves from a quartz crystal. In the first experiments the ultrasonic beam was passed through a mixture of carbon dioxide or hydrogen and air contained in a brass tube with ends covered by the celluloid films. The intensity of the emergent beam was measured by the pressure it exerted against a torsion vane and it was found that there was a nearly logarithmic decrease in the intensity with an increase in the percentage of the gas.[2] The experiments have been continued with a new form of absorption tube which greatly diminished the resonance effect and which allowed the determination of the absorption curves for two different lengths of tube with the same films at the ends.

Apparatus

The arrangement of the apparatus is shown in Fig. 1. C_1, the source of the waves, was a piezo-electric quartz crystal, connected to an oscillating

[1] G. W. Pierce, Proc. Am. Acad. Arts & Sci. **60**, 298 (1925).
[2] T. P. Abello, Proc. Nat. Acad. Sci. **13**, 699 (1927).

circuit as shown. The crystal radiated waves with a frequency of 612 kilocycles as determined by the electrical frequency of the oscillator. The oscillator was completely shielded except for the window O, of about 2 cm diameter, in the metal wall W. Emerging from O, the waves passed through the absorption tube A, the ends of which were covered by thin celluloid films, then through one of the holes, also covered with film, in the metal disk D, and finally struck the face of the receiving crystal C_2. The pressure of the waves induced an alternating potential of the same frequency as the incident waves on the opposite faces of the crystal. This signal was impressed on the grid of the first tube. It was then heterodyned, amplified and, by a second transformer, applied to the grids of the last two tubes which were connected in parallel. The negative grid bias on these tubes

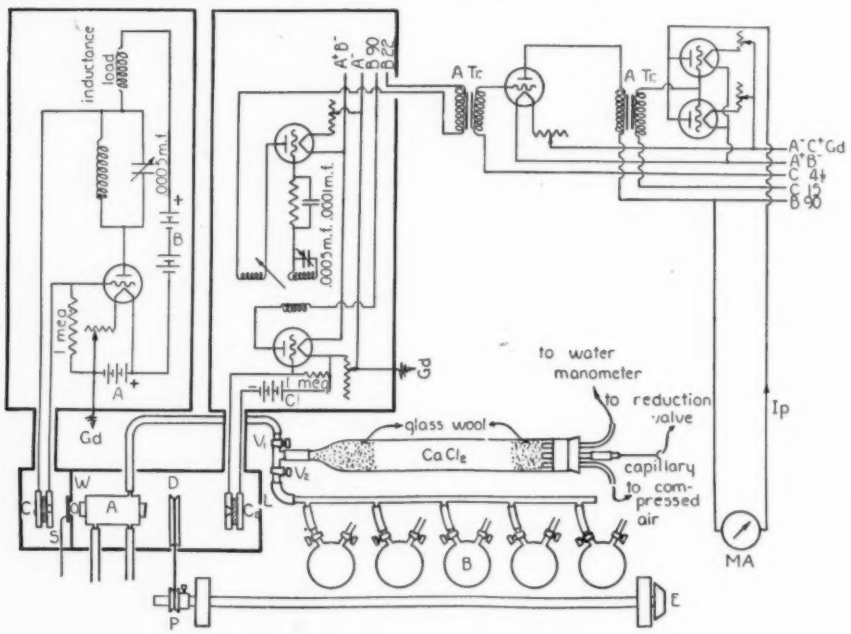


Fig. 1. Diagram of apparatus.

was so adjusted that they were operating near the foot of the I_p-E_g characteristic curve, so that when O was closed by means of the bakelite shutter S thus stopping completely the waves, the milliammeter MA read nearly zero. They thus acted as a peak voltage voltmeter. All the tubes (UV 201A) were mounted on cushions and the metal shields were supported on corks to absorb vibrations. By means of two brass stopcocks V_1 and V_2 the mixture of the gas and air, coming from the $CaCl_2$ tube, could be passed either through A or through any of the glass balloons B. A ten-liter bottle was inserted between the compressed air pipe and the drying tube to keep the flow of air constant. The composition of the mixture was altered by changing the pressure in the reduction valve which was placed before a capillary.

Crystal and mountings. The two crystals which were cut from the same natural crystal, were of the same shape and very nearly the same thickness. They were ground to have nearly the same natural frequency. It was found that they vibrated more strongly when the opposite faces were polished with fine rouge. In the experiment the waves were propagated in the direction of the electric axis. The crystals were held between brass electrodes and by increasing the pressure on the crystal its frequency could be varied within a small range. The electrodes had circular holes, about 1.5 cm in diameter, opposite the center of the crystal, through which the waves passed. For the receiving crystal the edges of the hole were bevelled at about 45° to prevent reflected waves striking the crystal.

The absorption tube. The absorption in various gases was observed by introducing them into a tube through which the sound passed. The ends were closed by thin celuloid films, so that the two crystals always oscillated in air,

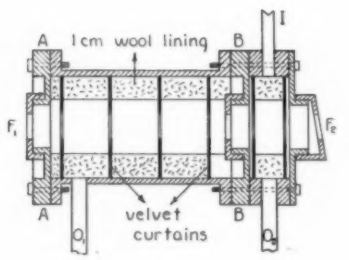


Fig. 2. Absorption tube.

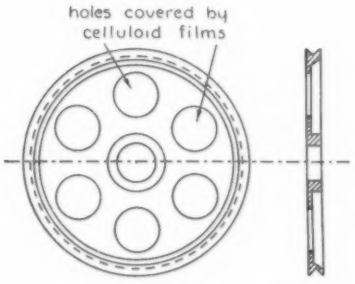


Fig. 3. Calibration disk.

no matter what gases were being studied. Fig. 2 shows a section of the absorption tube used. It was a brass tube having the inside lined with a 1 cm layer of wool. Along the entire length, placed at nearly regular intervals, were velvet curtains which limited the beam to a diameter of 1 cm. The holes in the caps F_1 and F_2 which were held on by wax, were covered with thin celluloid films formed on a clean mercury surface. To test whether the film was air-tight, the cap was inverted in a vessel and enough water was poured in until the confined air was under about 0.5 cm difference of pressure. The film bulged out a little and if the bulging remained for several hours the film was considered sufficiently tight. The film at F_2 was placed not exactly normal to the direction of the beam but inclined at a small angle. In that position reflection from it was towards the velvet curtains and wool linings where it would be dissipated by multiple reflections, instead of towards the other film. This form of tube greatly reduced, although it did not completely eliminate, resonance. This is important for since the wave-length inside the tube changed with the change in the composition of the mixture while the length of the tube was constant, the tube would be in resonance for certain mixtures but not for others. The tube was made so that it could be used to give two different lenths of absorbing gas leaving the geometrical arrangement of openings and absorbing screens the same.

This was done by interchanging the sections AA and BB. The new position of the film F_1 made a tube length of only 3.5 cms for the gas mixture which entered at I and left at O_2. In the arrangement shown the tube length F_1F_2 was 10 cms and the gas mixture entered at I and left at O_1. To make the joints air-tight, rubber washers were placed between sections.

The calibration disk. The brass disk D used to determine the intensity transmitted was about 9 cm in diameter. It had six circular holes 1.5 cm in diameter, with their centers equally spaced on a circle 5 cm in diameter. The holes were covered with celluloid films of different thicknesses, formed on a clean surface of water. These films were very much thinner than those at the ends of A. The two thinnest were white while the others showed interference colors. They were, however, very porous and so could not be used to cover the ends of A. As shown in Fig. 3, the edge of D was grooved so that by means of a pulley and rod it could be rotated from E (Fig. 1). In this way one could place in succession the various films in the path of the beam and at the same time read the milliammeter MA. The transmitting powers of these films were previously determined so that the reading of MA could be expressed in terms of the intensity of the beam striking the face of the receiving crystal.

Determination of Transmitting Powers of Films

It was thought at first that the transmission through these films could be obtained from Rayleigh's formula, and their thicknesses were therefore determined by an interferometer. It turned out however that the transmission through them as measured by a torsion vane was very much less than the value computed from Rayleigh's formula. It was therefore decided to use the transmission, as measured by the torsion vane, in this work. This was done in the following way. Referring to Fig. 1, the absorption tube A and the receiving crystal C_2 were removed from the box, the inside of which was lined with a 0.5 cm layer of wool, to absorb waves striking it. At the same position occupied by the face of the receiving crystal, a very thin circular mica vane of the same size as the hole in the electrode was suspended, with its plane vertical, from a graduated torsion head by a quartz fiber 0.002 cm thick and 15 cm long. Fig. 4 shows how the vane was suspended. The suspension and vane were completely shielded from air currents except for the two small holes through which the string, used to rotate D, passed. The amount of rotation which was required to restore the vane to its original position was taken as a measure of the intensity of the beam. All the holes were covered with films, the transmission through the thinnest that could be made being about 30 percent of the transmission through an uncovered hole.

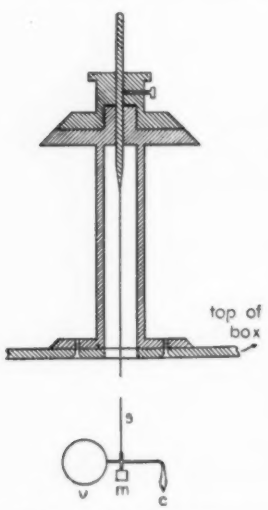


Fig. 4. Torsion vane.

Different series of measurements gave very consistent values for the amount transmitted by the various films. Taking the transmission through the thinnest as 100, the values for the others are 79.1; 52.6; 42.1; 29.6 and 7.8.

Measurement of the Absorption

In making an absorption measurement, the curve connecting the milliammeter readings with the intensity of the waves striking the face of the receiving crystal was first taken by placing the various films in the path of the beam. The disc D was left with the thinnest film in the path of the beam. Fig. 5 shows such a calibration curve which we will refer to as an I_p-Intensity curve; the intensity transmitted by the thinnest film with air in the absorption chamber being arbitrarily taken as 100.

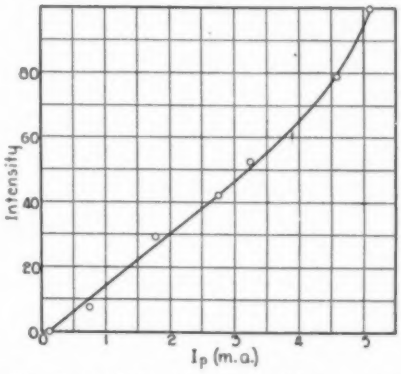


Fig. 5. I_p-Intensity calibration curve.

A little gas was then allowed to mix with the air. The milliammeter reading dropped slowly and after a while, generally about 1.5 minutes, when the mixture flowing through A had become constant, as indicated by the constant reading of MA, the readings of MA, the reduction valve, and the water manometer were recorded. Then the rate of flow of the gas was increased by increasing the pressure in the reduction valve and the above process was repeated. Superimposed on the gradual decrease in the ammeter reading with increasing proportion of added gas, there was a fluctuation of small amplitude caused by the recurrence of resonance as the mixture reached certain proportions. This effect was most prominent with hydrogen and helium and was hardly noticeable in carbon dioxide and other gases with high absorption. In a run five different mixtures were used. After the readings for the last mixture were taken, the flow of the gas was stopped and MA was read again for pure air to be sure that the circuits had not changed during the interval (generally about 12 minutes). If the run was good, sections AA and BB of the tube A were interchanged, the I_p-Intensity curve was determined again for this new setting, and the above procedure was repeated for the shorter tube using the same percentage mixtures as those which had been used with the longer tube. Finally samples, corresponding to the different mixtures used, were taken. To do this the valve V_1 was closed and V_2 was opened and the mixture was allowed to pass through one of the glass balloons, B. The reduction valve was adjusted so that it read the pressure used before and by means of V_2 or the inlet valve of the glass balloon, the rate of flow of the mixture was regulated so that the water manometer gave the corresponding reading. The bulbs containing the samples of the mixtures were then weighed on an analytical balance and the volume percentage of the mixture was determined from the I_p-Intensity curve.

It is evident that when the percentage of the mixture inside A is changed, the fractional part of the beam which is reflected from the films also changes. It was in order to eliminate this correction experimentally that the absorption curves for two different lengths were determined. If x is the percentage (by volume) of the gas in the mixture, there is a certain function $f(t,x)$ of x and the thickness t, which gives the fractional part of the energy transmitted by the films at the ends of the absorption tube. In the tube the absorption coefficient of the mixture $\mu(x)$ depends on x. The intensity at the receiving crystal, I_{1x} with a tube of length l_1 will depend on x according to a formula of the type $I_{1x}=Af(t,x)e^{-\mu(x)l_1}$. The experiments agree with the relation $\mu(x)=\mu(0)+kx$, giving for the dependence on x,

$$I_{1x}=I_0 f(t,x)e^{-kl_1x} \tag{1}$$

where I_0 is a constant. The coefficient $k=[\mu(x)-\mu(0)]/x$ is the difference in the absorption coefficient of pure air and of a mixture containing 1 percent by volume of the gas studied.

If the length of the tube is increased to l_2, the transmitted intensity with the same mixture and the same films is $I_{2x}=I_0 f(t,x)e^{-kl_2x}$. By division we get

$$I_{2x}/I_{1x}=e^{-klx} \text{ or } \log (I_{2x}/I_{1x})=-klx$$

where $l=(l_2-l_1)$ is the difference in the length of the two tubes. Therefore by dividing the ordinates of the absorption curve for the longer tube by the corresponding ordinates of the curve for the shorter tube (intensity is the ordinate) the effect of reflection at the gas surfaces could be eliminated, and what we obtain is the true absorption curve due to the difference in length. From this curve the value of k is readily determined. Moreover we see that once the value of k is known we can also learn something about the dependence of $f(x,t)$ on x. For from (1) we get

$$I_0 f(t,x)=I_{1x}e^{kl_1x}$$

giving the dependence of the transmission function $f(t,x)$ on the percentage of gas in the mixture.

Results and Discussion

Carbon-dioxide and nitrous-oxide. These two gases showed exactly similar behavior (Figs. 6 and 7). Both absorbed the waves very highly and for them the function $f(t,x)$ increased with x, which means that the fractional part of the incident waves which was transmitted by the films increased as the percentage of the gas in the mixture was increased. The coefficient k in (1) may be deduced from the curves. When the length is in centimeters, and x is the percent by volume, k for CO_2 is 0.029 and for N_2O is 0.034.

Hydrogen and helium. The curves (Fig. 8 and 9) obtained for hydrogen and helium are similar although the helium curves show very much less absorption than those for hydrogen and there seemed to be a tendency for

the helium curves for the two different lengths of tube to come together at high percentage. But I would not emphasize this fact as the experimental error at low intensity was proportionately great. There is, however, a very

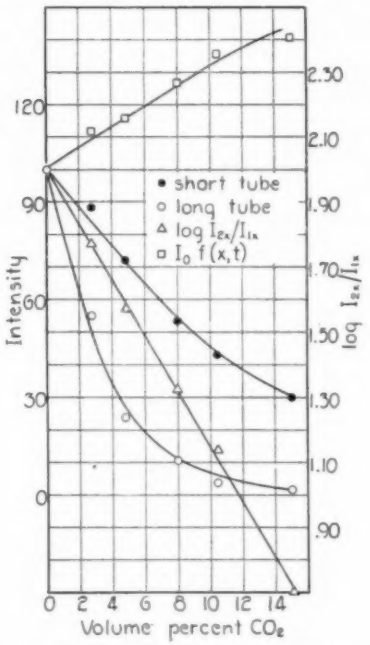


Fig. 6. Variation of intensity with volume-percent of CO_2.

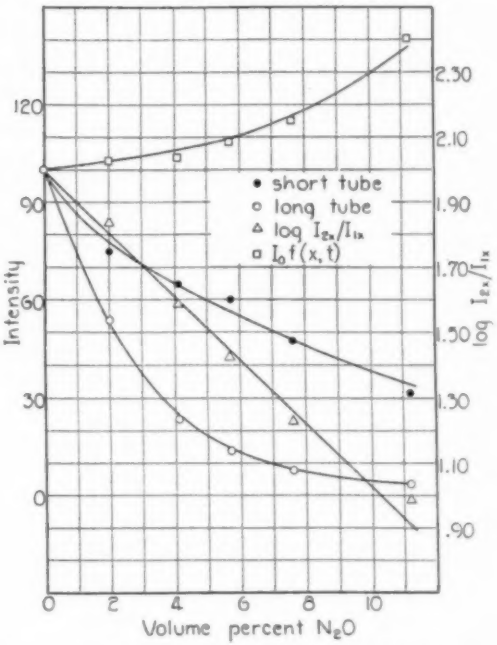


Fig. 7. Variation of intensity with volume-percent of N_2O.

striking contrast between the behavior of these two lighter gases and the behavior of carbon dioxide and nitrous oxide, namely, that for hydrogen and helium $f(t,x)$ is a decreasing function of x, while for the other two, it is

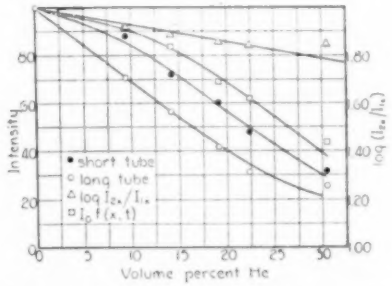


Fig. 8. Variation of intensity with volume-percent of He.

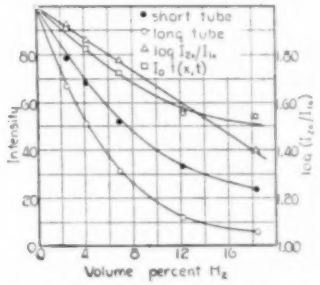


Fig. 9. Variation of intensity with volume-percent of H_2.

an increasing function. We shall come to this fact again later. In the case of helium this new method of determing the absorption curves for two different lengths of tube showed that much of the decrease in intensity

[3] T. P. Abello, Phys. Rev. **31**, 157 (1928).

previously reported[3] was due to the increase in reflection at the gas surfaces. The value of the coefficient k for H_2 deduced from Fig. 9 is 0.014 and for He deduced from Fig. 8 is 0.0025.

Argon. In experiments with this gas a slow current of argon was allowed to flow into the tube A thus slowly increasing the percentage of the mixture. Apparent absorption was noticed at certain concentrations, but on closing the inlet and outlet of A the absorption disappeared almost instantly, indicating that the apparent absorption was due to scattering caused by the inhomogeneity of the mixture. With pure argon the milliameter reading was the same as with pure air.

Ethylene. No quantitative measurement of the absorption in ethylene was made because the percentage of the mixture could not be determined by the difference in weight. However, this gas was also tried and a rough idea of its behavior was obtained by plotting the intensity against the pressure of the reduction valve. With the lean mixtures used in the experiment, the percentage of the gas would be nearly proportional to this pressure. From the relative slopes of the curves obtained for short and long tubes, it seemed as if the absorption in this gas is of the same order of magnitude as the absorption in CO_2 and N_2O.

Transmission by Films from a Rare to Dense Medium

Let us now return to the discussion of the observed behavior of the function $f(x,t)$. Extending the method used by Rayleigh to determine the energy of the transmitted and reflected waves at a thin infinite surface with the same medium on both sides, to the case of different media, we obtain the following expression for the reflected energy:

$$\text{Reflected energy} = \frac{\cot^2 a_2 l\left(\frac{\rho_3}{\rho_1}-\frac{a_3}{a_1}\right)^2+\left(\frac{v_1\rho_3}{v_2\rho_2}-\frac{v_2\rho_2}{v_3\rho_3}\right)^2}{\cot^2 a_2 l\left(\frac{\rho_3}{\rho_1}-\frac{a_3}{a_1}\right)^2+\left(\frac{v_1\rho_3}{v_2\rho_2}+\frac{v_2\rho_2}{v_3\rho_1}\right)^2} \tag{3}$$

where $a=2\pi/\lambda$, λ is the wave-length, ρ, the density, l, the thickness of the second medium, and v, the velocity of the waves. The subscripts 1, 2, and 3 refer to the first, second, and third medium respectively, In this experiment, l was the thickness of the film and since $l \ll \lambda_2$, $\cot^2 a_2 l = (\lambda_2/2\pi l)^2$ very approximately. Furthermore we can write

$$\frac{v_1\rho_3}{v_2\rho_2}-\frac{v_2\rho_2}{v_3\rho_1}=-\frac{v_2\rho_2}{v_3\rho_1}$$

very approximately since $v_1v_3/v_2^2 \ll \rho_2^2/\rho_1\rho_3$. Introducing these approximations, the reflected energy becomes

$$\text{Reflected energy} = \frac{\left(\frac{\beta-1}{2}\right)^2+\left(\frac{\pi l\rho_2}{\lambda_1\rho_1}\right)^2}{\left(\frac{\beta+1}{2}\right)^2+\left(\frac{\pi l\rho_2}{\lambda_1\rho_1}\right)^2} \tag{4}$$

where $\beta = v_3\rho_3/v_1\rho_1$. When the third medium is the same as the first medium the above formula reduces to Rayleigh's formula. (Theory of Sound, II, p. 88).

$$\text{Reflected energy} = \frac{(\pi l\rho_2/\lambda_1\rho_1)^2}{1+(\pi l\rho_2/\lambda_1\rho_1)^2} \tag{5}$$

Interchanging subscripts 1 and 3 in Eq. (3) we also find expression (4) for the reflected energy, showing that the fraction reflected is the same for waves incident in the first medium as for waves incident in the third medium and that the effect of our two films is the same as double tramsmission from air through the film into the mixture.

Now a close examination will show that Eq. (4) is greater than Eq. (5) for $[(2\pi l\rho_2/\lambda_1\rho_1)^2+1] < \beta < 1$ but is less than Eq. (5) for $[(2\pi l\rho_2/\lambda_1\rho_1)^2+1] > \beta > 1$. In the experiment β cannot be greater than $[(2\pi l\rho_2/\lambda_1\rho_1)^2+1]$. In other words the reflected energy will always be greater for any third medium satisfying the condition $\beta < 1$ than for the same medium on both sides. The reverse will be the case for the transmitted energy. Using the velocity of audible waves for lack of experimental data since very little has been done on the velocity of high frequency waves, we see that with air as the first medium, β is less than 1, when hydrogen, helium or their mixtures with air form the third medium. The opposite is the case with carbon-dioxide and nitrous-oxide. Hence the experimental curves for $f(x,t)$ agree at least qualitatively with Rayleigh's theory on the above supposition.

An increase of velocity in CO_2, as observed by Pierce for 206 kilocycles, would still further increase the theoretical transmission in CO_2. Hitchcock,[4] however, reported recently that the velocity of the waves from a vibrating crystal is a function of the energy which the crystal radiates, and he obtained a value in air nearly twice the velocity of ordinary sound waves. If this is the case, undoubtedly the velocity in other gases will also be very different from the velocity of ordinary waves. Experiments along this line are very desirable.

The writer wishes to take this opportunity to express his indebtedness to Professor A. J. Dempster who had suggested this investigation, for his valuable advice and criticisms throughout the progress of the work. He also wishes to thank Dr. Barton Hoag for helping him in cutting the crystals and Mr. Fred Pearson of the optical shop for the final grinding and polishing of them.

RYERSON PHYSICAL LABORATORY,
UNIVERSITY OF CHICAGO.
March, 1928.

[4] R. C. Hitchcock, Proc. Inst. R. E. **15**, 906 (1927).

THE VIBRATION OF BELLS

By Arthur Taber Jones

Abstract

Relative frequencies, nodal meridians, and nodal circles of the bells of the Harkness Memorial Chime.—This is a study of the ten bells of the Harkness Memorial Chime at Yale University. The large size of these bells makes it possible to examine partial tones of higher order than could be studied on smaller bells. For the first ten partials the average values found for the relative frequencies, the numbers of nodal meridians, and the numbers of nodal circles are shown in the following table.

Partial	1	2	3	4	5	6	7	8	9	10
Relative Frequency	0.50	1.00	1.20	1.49	2.00	2.56	2.96	3.28	3.80	4.06
Nodal Meridians	4	4	6	6	8	8	10	8	10	12
Nodal Circles	0	1	1	1	1	2	2			

The nodal circles for the 2d, 3d, 4th, and 5th partials are at levels about 1/3, 1/2, 1/6, and 1/2 the height of the bell, those for the 6th partial are roughly at 1/5 and 3/5, for the 7th at 2/5 and 4/5 of the height.

Amplitudes of the partials.—Curves showing the vibration in the air near the bells were obtained by a microphone, amplifier, and oscillograph. There is first an irregular motion which may arise from noises in the mechanism by which the bells are struck. The clapper probably strikes after some 0.01 sec. to 0.03 sec., for after this time the amplitude is larger and the curve more regular. Since the partial tones of a bell are not harmonic a Fourier analysis is not directly applicable, but a *modified Fourier analysis* may be employed. An approximation to the amplitude of each component is obtained by proceeding as if a Fourier analysis were being made, the range of integration for each component being however independently chosen as a whole number of periods of that component. A method is given for obtaining corrections to the approximate amplitudes thus found.

The strike note of bells.—The curious phenomenon of the *strike note* is considered. The hypothesis that the pitch of the strike note is determined by that of the fifth partial, but that it is very generally judged an octave lower, is supported by several facts which have been already known and by the new fact that the fifth partial appears with surprising promptness and vigor. One possible cause for such a misjudging of the octave is the fact that the fifth, seventh, and tenth partials are all brought out well when a bell is struck on the soundbow, and that the relative frequencies of these partials are not far from 2:3:4, thus perhaps giving rise in the ear of the observer to the pitch of the strike note.

Introduction

THE vibrations of bells are not well understood. Even on so elementary a matter as the number and position of nodal lines the very meager published values are not in satisfactory agreement. Moreover the different partial tones of a single bell usually bear inharmonious relations to each other, and the relative frequencies of the partial tones in one bell often differ from the relative frequencies in other bells—even when the bells were cast

by the same founder. As to the frequencies which it is desirable for the partials to have, there seems now to be more or less agreement[1] that in the best bells the first seven partials have frequencies in the ratio 1:2:2.4:3:4:5:6, although the third partial is sometimes represented by 2.5 instead of 2.4, being thus a major third above the second partial instead of a minor third above it.[2]

In addition to the partials of a bell certain other tones can be heard. The most important of these is called the "strike note." The strike note is the most prominent note heard when bells are sounded in fairly rapid succession. It is usually this note that it meant when the pitch of a bell is given. Griesbacher[3] states that the strike note is audible at distances at which none of the partial tones can be heard. In bells that are well tuned the strike note coincides with the second partial, but in most cases the two tones differ in pitch, often to the extent of a major second or more. If a tuning fork has nearly the pitch of a partial tone, beats are easily detected; but no beats can be obtained from a fork and the strike note. The strike note is not a combination tone, and Blessing[4] states that when sounding with other notes it is not capable of producing combination tones. The partial tones are produced, as we should expect, by division of the bell into various numbers of transversely vibrating segments separated by nodal lines. The strike note appears to be produced in some other way. The partial tones can be elicited by resonance, and when a bell has been struck they can be reinforced in the usual manner by Helmholtz resonators. The strike note is not reinforced by a resonator, and Biehle[5] has even called it an "imaginary tone." Neither is it easy to obtain the strike note by resonance. A tuning fork may be adjusted until its pitch is that of one of the partial tones of a bell. If the fork is then struck and its stem pressed against the bell the partial tone comes out very clearly. When the strike note has a pitch different from that of the second partial it is not easy to obtain any such response from the strike note. Griesbacher[6] has found however that by tuning a fork to the pitch of the strike note, setting the fork into vibration, and then pressing either

[1] J. Biehle, Archiv für Musikwiss. **1,** 306 (1919); W. W. Starmer, Beiaardkunst, Handelingen van het Eerste Congress, p. 69, Mechelen (1922); William Gorham Rice, Carillons and Singing Towers of the Old World and the New, p. 226, Dodd, Mead, and Company (1925); P. Griesbacher, Glockenmusik, pp. 14, 23, Alfred Coppenrath (1927).

[2] It is possible to tune the partial tones of a bell to some extent by cutting out material from the inside of the bell at different levels. This fact was known in the seventeenth century to the two Hemony brothers, who cast bells that are still famous for the quality of their sound. But the art was lost and not rediscovered until some thirty years ago. The rediscovery was made independently by Canon Simpson (Pall Mall Magazine, Oct., 1895, and Sept., 1896) and more recently by Johannes Biehle. Simpson's method has been developed by John Taylor and Company of Loughborough, England, and Gillett and Johnston of Croydon, England. So far as I know, all of the dozen or more carillons that have been installed in this country and Canada during the past four or five years have been cast by one or the other of these two firms.

[3] Griesbacher, ref. 1, p. 40.

[4] P. J. Blessing, Phys. Zeits. **12,** 597 (1911).

[5] Biehle, ref. 1, p. 296.

[6] Griesbacher, ref. 1, pp. 53–55.

the stem or the lowest part of a prong against the lip, where the inner and outer surfaces of the bell meet, it is possible to obtain the strike note.[7]

Griesbacher appears to think[8] that in the production of the strike note the metal on the inner and outer sides of the soundbow, on which the clapper strikes, vibrates in opposite directions. That would seem to mean that the waves which produce the strike note are compressional rather than flexural. But this explanation seems to be ruled out[8] by work which I did[9] some years ago on the Dorothea Carlile Chime at Smith College. Moreover if the strike note were due to such compressional waves it would seem that it should be possible to pick it up by a Helmholtz resonator held just beyond the lip in the region where flexural vibrations of the bell would give a minimum of intensity. I do not find this to be the case.

In a number of bells which Rayleigh[10] examined he found that the strike note was an octave below the fifth partial.[11] Biehle[12] and Griesbacher,[13] both of whom have examined many bells, state that the strike note is almost always an exact octave below the fifth partial, but that in rare cases there are slight deviations from this relationship. In my study of the Dorothea Carlile Chime I found the strike note an octave below the fifth partial, and I suggested as a possible explanation of the strike note that the fifth partial may perhaps come out with especial promptness and prominence, the octave in which it lies being however very generally misjudged.[14]

[7] Griesbacher states that he has been able in this way to obtain the strike notes of hundreds of bells. His book did not reach me until most of the experimental work reported in this paper had been completed. I was skeptical about the possibility of getting the strike note to respond to a tuning fork, but I have succeeded on two bells in verifying his statement that it is possible. I have also succeeded in getting the strike note to respond by holding the fork at an oblique angle to the surface of the bell, and then touching the stem lightly to the soundbow. If my explanation of the strike note as a misjudged octave is correct, I do not see why this effect should be obtained.

[8] Suppose that we have a bell and also a ring made of bell metal. Then from measurements on particular bells it is not difficult to show (See ref. 9 and Lamb, Dynamical Theory of Sound, ed. of 1910, p. 136) that if the ring is to vibrate in the compressional mode which has the lowest frequency, and if the frequency of the ring is the same as the strike note of the bell, then the diameter of the ring must be nearly three times the diameter of the mouth of the bell. Now it is true that the normal modes of vibration for a ring differ from those for a bell, but it hardly seems likely that for compressional modes of the same frequency the dimensions would differ so widely.

[9] A. T. Jones, Phys. Rev. **16**, 247 (1920).

[10] Rayleigh, Phil. Mag. **29**, 1 (1890), and Theory of Sound, ed. 2, vol. 1, p. 393.

[11] The statements in Rayleigh's paper in the Philosophical Magazine have been quoted (Winkelmann, Hdbuch d. Physik, ed. of 1909, vol. 2, p. 405) and seemed to indicate that the strike note was usually two octaves lower than the fifth partial, but in his treatment of the same question in the Theory of Sound he is careful to state definitely that "the nominal pitch, as given by the makers, is an octave below" the fifth partial.

[12] Biehle, ref. 1, pp. 299–300.

[13] Griesbacher, ref. 1, pp. 54, 57.

[14] Cases of error in the judgment of an octave are not uncommon. Helmholtz states (Sensations of Tone, tr. Ellis, ed. 4, p. 62) that when Tartini discovered combination tones he gave the pitch an octave too high, and that Henrici gave for some of the partial tones of tuning forks pitches an ocatve too low. Rayleigh states (ref. 10, p. 5) that "pure tones are often

The work described in this paper was undertaken in the hope that it would clear up some of the discrepancies as to the nodal lines of bells, and would also contribute to an understanding of the strike note. This latter purpose was to be attained by securing information as to the relative intensities of the different partials, and especially by finding out whether the fifth partial really is very prompt and vigorous. Most of the work was carried out on the bells of the Harkness Memorial Chime[15] at Yale University.

The Frequencies of the Partials

The frequencies of the partials were determined by counting the beats which they made with notes from a vacuum tube oscillatory set. This set was calibrated by comparison with thirteen tuning forks made by König, and during the work on the bells the oscillator was compared frequently with a tuning fork of known frequency. The frequencies obtained are not as reliable as had been hoped. They can probably be trusted to one percent.

The results are summarised in Table I, which also includes a summary of the corresponding results from the earlier work on the Dorothea Carlile

Table I. *Relative frequencies of the partials.* The frequencies are calculated with reference to the fifth partial, and the frequency of the fifth partial is taken as 2, so as to make the frequency of the strike note equal to 1.

Partial	Ideal Ratios	Dorothea Carlile Chime			Harkness Chime		
		No. of Bells Examined	Av.	Av. Dev.	No. of Bells Examined	Av.	Av. Dev.
1	0.50	12	0.58	0.010	10	0.50	0.004
2	1.00	12	0.92	0.037	10	1.00	0.008
3	1.20	12	1.19	0.016	10	1.20	0.013
4	1.50	12	1.71	0.023	10	1.49	0.014
5	2.00	12	2.00		10	2.00	
6	2.50	6	2.74	0.069	10	2.56	0.045
7	3.00	6	3.00	0.028	10	2.96	0.022
8	3.33				7	3.28	0.036
9	3.75	2	3.77	0.177	7	3.80	0.113
10	4.00	1	4.07		7	4.06	0.052

Chime. It will be seen that the relative frequencies of the first five partials on all the bells of the Harkness Chime are very close to those indicated above as given by the best bells. The tenth partial is about an octave above the fifth, and the seventh, eighth, ninth, and tenth do not differ widely from the series *sol*, *la*, *ti*, *do*. If these values were precise, and we use a scale that is not tempered, the relative frequencies of the first ten partials of an ideal bell would be those given in the second column of the table.

estimated by musicians an octave too low." Obata (Frank. Inst. Journ. **203**, 659 (1927)) has recently found that the sounds from the striking of bricks and from xylophones "give a feeling of sounds about two octaves lower than those determined by the oscillographic records."

[15] The Harkness Memorial Chime consists of ten bells cast in 1921 by John Taylor and Company. The largest bell is $f\#_2$, with a strike note of about 182 cycles/sec. It weighs about 6300 kg, and has a maximum diameter of 219 cm. The smallest bell is g_3, of about 385 cycles/sec. This bell weighs about 680 kg, and has a maximum diameter of 104 cm.

Nodal Lines

General considerations. Two systems of nodal lines are generally recognized in bells. One is a system of meridians which run up and down the bell at different azimuths, and the other is a system of circles which lie at different levels. Rayleigh[10] and Vas Nunes[16] examined a few of the nodal lines on a few bells. Biehle[12] has examined the partial tones of several hundred bells, and has published some brief statements about nodal lines. van der Elst[17] is developing a bar resonator which is intended in part for studying the nodal lines of bells, but I think he has as yet published nothing as to results obtained with it.

On the Harkness Chime I have examined the nodal lines in practically the same way that I described in connection with the work on the Dorothea Carlile Chime.[9] That is, I connected a Helmholtz resonator through a piece of rubber tubing to the binaurals of a stethoscope, tuned the resonator by covering the mouth to a greater or less extent with a finger, moved the resonator about near the surface of the bell, and listened for the positions of minimum intensity.

Nodal meridians. The numbers of nodal meridians which I found for the first ten partials on the bells of the Harkness Chime are shown in Table II.

TABLE II. *Nodal lines.* The positions of the nodal circles are indicated by fractions. The unit chosen is the distance measured along the outer surface of the bell from the lip to the shoulder. Numbers in parentheses give average deviations. The middle of the soundbow, on which the clapper strikes, is at 0.12 (0.007). Except where otherwise noted the results are from observations on all of the bells.

Partial	No. of Nodal Meridians	No. of Nodal Circles	Location of Nodal Circles	Remarks
1	4	0		
2	4	1	0.32 (0.037)	
3	6	1	0.53 (0.010)	Position of circle determined on all bells except two of the largest.[18]
4	6	1	0.16 (0.026) 0.15 (0.010)	These two values were obtained by measuring along the outer and inner surfaces of the bells.
5	8	1	0.47 (0.045)	
6	8	2	0.21 (0.022) 0.55 (0.021)	
7	10	2	0.43 (0.031) 0.76 (0.067)	Locations of these two circles are avs. for all except the two smallest bells.
8	8			
9	10			
10	12			

[16] Abraham Vas Nunes, Experimenteel Onderzoek van Klokken van F. Hemony, pp. 95–97. Dissertation, Amsterdam (1909).

[17] W. van der Elst, Physica, **6**, 42 (1926).

[18] Most of the determinations of the location of the nodal circle for the third partial were made after the rest of the work was completed and ladders had been removed from the tower. See footnote 21.

These numbers agree with those which I found on the Dorothea Carlile Chime.[19] My results agree with those of Rayleigh up to the fifth partial. The largest bell that he used was considerably smaller than the smallest on the Harkness Chime, so that for higher partials he was not able to examine nodal meridians. Biehle gives numbers of nodal meridians for the first eight partials. For the first seven my results agree with his.[20] My results do not agree entirely with those of Vas Nunes. But not only did Vas Nunes work without resonators—which makes any determination of this sort very difficult—but the series of frequencies which he found is somewhat different from the series that I have found, and it may be that there are also differences in the nodal lines.

Nodal circles. The nodal circles are more difficult to locate than the meridians. My results for the first seven partials are given in Table II. On comparing with Table I in my former paper it will be seen that there is good agreement, and that on the Harkness Chime I have been able to locate circles for the fourth and seventh partials in regions of the bells where I was not able to detect those partials on the smaller bells of the Dorothea Carlile Chime. In the case of the fourth partial there is a nodal surface that cuts through the material of the bell in the neighborhood of the sound-bow. Mechanically it seems remarkable to have a surface of minimum transverse motion so close to a parallel free edge.

Biehle[12] gives the numbers of nodal circles for the first eight partials as 0, 1, 0, 1, 0, 1, 0, 1. It will be seen that except for the first, second, and fourth partials my numbers do not agree with his. For any one partial Vas Nunes[16] was not able to detect more than one nodal circle, although he supposed that the higher partials would have more. Since the partials which he found differ from those which I found, it is somewhat difficult to compare results. But in so far as I am able to compare tones that seem to correspond, the results for the nodal circles appear to agree. Rayleigh[10] gives results as to nodal circles for the first four partials. His results are definite for only the first two, but in no case is there disagreement between his results and mine.[21]

[19] Comparison with my former paper does not show agreement in the numbers of nodal meridians for the highest partials. In preliminary work on the Harkness Chime I missed the eighth partial, and it turns out that in the study of the Dorothea Carlile Chime I also missed it. On checking over the higher partials on the two largest bells of the Dorothea Carlile Chime—the only ones on which I was able to detect partials higher than the seventh—I have found this eighth partial, and I now find that the numbers of nodal meridians on the Dorothea Carlile Chime—so far as I am able to examine them—agree with those which I have found on the Harkness Chime.

[20] For the eighth partial Biehle gives ten nodal meridians—the same number that I published for the Dorothea Carlile Chime when I thought that the ninth partial was the eighth.

[21] In the case of the third partial Rayleigh gives a result for one bell. He says, "There is no well-defined nodal circle. The sound is indeed very faint, when the tap is much removed from the sound-bow; it was thought to fall to a minimum when the tap was about halfway up." In my paper on the Dorothea Carlile Chime I indicated that the third partial has one nodal circle. On the Harkness Chime I had great difficulty in deciding whether this partial really has a nodal circle or not. There was no doubt that the note heard in a resonator tuned to this partial disappeared and then reappeared when the resonator was moved up and down along the

I have not found the nodal circles for partials higher than the seventh. But I may note that the first, second, third, fifth, seventh, and tenth partials are well brought out by tapping on the soundbow, whereas the fourth, sixth, eighth, and ninth are better obtained by tapping higher up. The eighth and ninth are separated by tapping at slightly different levels on the waist of the bell. These facts may perhaps mean that when a bell is struck by the clapper the fourth, sixth, eighth, and ninth partials do not come out as strongly as the others, so that in tuning a bell especial care should be given to the first, second, third, fifth, and seventh partials.[22]

The Amplitudes of the Partials

Experimental arrangement. Curves representing the sounds from the different bells were obtained by using a high quality microphone, an amplifier, and an oscillograph with recording camera. The accuracy of transmission was tested by holding successively near the microphone three tuning forks which differed considerably in pitch, each provided with the proper resonator. The distortion proved not to be important. The speed at which the photographic film moved was obtained by records from current in a shunt around an electrically driven tuning fork. But as the oscillograph which was available had only a single vibrator, curves from the fork and a bell could not be taken at the same time, and this casts some doubt on the accuracy of the timing.

Analysis of the curves. Since the periods of the partial tones of a bell do not form a harmonic series, a Fourier analysis of the curves is not directly applicable. The method finally adopted was the following. Some fifty to eighty equally spaced ordinates were measured and then multiplied by $\sin nt$ and $\cos nt$ respectively, where n stands for 2π times the frequency of some chosen partial tone. By adding these products approximations were obtained to the values of the integrals $\int y \sin nt\, dt$ and $\int y \cos nt\, dt$, the integration extending over a whole number of periods of the chosen partial. The amplitude was calculated as if a Fourier analysis were being made. The process was repeated for other sets of ordinates, so that from two to five values for the amplitude were obtained. The results were then averaged. The values obtained are in error, partly because of experimental inaccuracies

waist of a bell. But I came to think that this effect was due to the second partial overpowering the third in this region, and consequently stated, in a preliminary report on a part of this work (Phys. Rev. **29**, 616 (1927)), that the third partial has no nodal circle. When I attempted to check this over again on the Dorothea Carlile Chime I did not feel so sure, and after trying several methods that did not lead to the desired certainty I went back to Rayleigh's method of holding a resonator at one point while I tapped up and down the bell. This method seemed to show rather definitely a nodal circle for the third partial, and after checking over again several of the bells of the Harkness Chime by this method I now feel fairly sure that the third partial does have a nodal circle after all.

[22] On the bells of the Harkness Chime the first few partials have been tuned, on the bells of the Dorothea Carlile Chime they have not. And it is interesting to see from Table I that on the Dorothea Carlile Chime the average ratios of the frequencies for the third, fifth, and seventh partials are close to the ideal values, whereas the fourth and sixth partials deviate widely from those values.

in determining the speed of the film and the frequencies of the partials, partly because of the slight distortion in the transmission from microphone to oscillograph, partly because of the approximation involved in finding the integrals, partly because the range of integration is not a whole number of periods for partials other than the one in question, and probably partly because of an irregular motion to be mentioned shortly.

The error due to inharmonic relations between the partials may be corrected as follows.[23] Suppose at first that there are only two partials, and that the curve is represented by

$$y=a_1\cos n_1t+b_1\sin n_1t+a_2\cos n_2t+b_2\sin n_2t. \tag{1}$$

Let s be an integer, and let p be a quantity defined by the relation $sT_2=pT_1$, where $T_1=2\pi/n_1$ and $T_2=2\pi/n_2$. Then it is not difficult to show that

$$a_2=\frac{2}{sT_2}\int_0^{sT_2} y\cos n_2t\,dt-\frac{p}{\pi(p^2-s^2)}\left\{a_1\sin 2\pi p+b_1(1-\cos 2\pi p)\right\} \tag{2}$$

and

$$b_2=\frac{2}{sT_2}\int_0^{sT_2} y\sin n_2t\,dt+\frac{s}{\pi(p^2-s^2)}\left\{a_1(1-\cos 2\pi p)-b_1\sin 2\pi p\right\}. \tag{3}$$

From (2) and (3) it will be seen that if p is an integer the correction terms to the right of the integrals vanish, that if p is close to an integer these terms are small, and that if p and s are very different, i.e. if n_1 and n_2 are very different, these terms are small. When (1) contains more than two components each new component adds to (2) and (3) terms of the same form as the correction terms that have been written.

A first approximation is obtained by neglecting the correction terms in (2) and (3), a second approximation can be obtained by putting into the correction terms in the extended expressions which take the place of (2) and (3) the values found in the first approximation, and further approximations might be obtained by repeating the process. Results of applying these corrections are shown in Figs. 1 and 2. In Fig. 1 no important change is produced. In Fig. 2 the importance of the third partial is brought out more strongly, but the uncorrected values already indicated that it had the largest amplitude. The calculation of these corrections takes considerable time, and it has not been carried through except in these two cases.

Results. On curves which showed the beginning of the sound there was at first an irregular motion that lasted for from 0.01 sec. to 0.03 sec., and was followed by a considerable increase in amplitude and the development of a more regular type of vibration. In the initial irregular motion there was no evident periodicity, but there were suggestions of frequencies in the neighborhood of 1000 to 2000 or more cycles/sec. Such frequencies are higher than the tenth partials of the bells that were concerned, but not nearly high enough to arise from waves running back and forth through the ball of the

[23] I find that this method of correction is not new.

clapper. It is entirely possible that they may be due to noises in the mechanism by which the bells are struck. To what extent these irregular motions continued to be superposed on the more regular part of the curves I do not know.

Only a small number of satisfactory films were obtained, and the amplitudes have been calculated for only six. Three of these were exposed about the time a bell was struck, and in all three the analysis—beginning after the initial irregular motion—shows that the fifth partial has a considerably larger amplitude than the others. Fig. 1 shows the analysis of one of these films. On a few other films that were exposed when a bell was struck there was evident without analysis a prominent vibration which had a frequency about that of the fifth partial.

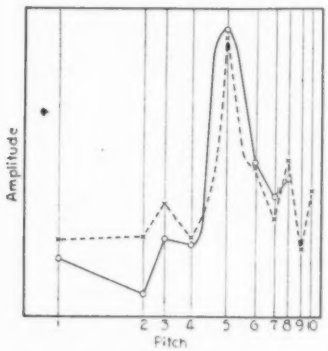


Fig. 1. Amplitudes of partials of a bell very soon after it was struck.

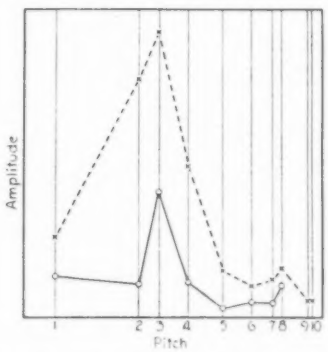


Fig. 2. Amplitudes of partials of another bell about 3 sec after it was struck.

In both these figures the abscissas are proportional to the logarithms of the frequencies, and the ordinates are proportional to the amplitudes. The numbers marked along the axes of abscissas indicate the partials. The scales for the amplitudes are arbitrary, and are different for the two figures. The points indicated by crosses and joined by dotted lines show the uncorrected amplitudes, and the points indicated by circles and joined by full lines show the corrected amplitudes.

A number of films were exposed about three seconds after the bells were struck. The general appearance of these films differs according to the size of the bell. For the three or four largest bells they show that several partials were still important. For the smaller bells they show that most of the partials had died down a good deal, leaving only one that had much amplitude. An examination of these films showed that the frequency of the tone that was now most prominent is about that of the third partial. Analyses were made of three of the films that were exposed about three seconds after the bells were struck. Two of these were cases where the curve showed only one prominent frequency, and in both of these cases the third partial does turn out to have a larger amplitude than any of the others. Fig. 2 shows one of these cases. The third curve was from one of the larger bells, and the analysis indicates that the third partial is prominent but does not have the largest amplitude.

This prominence of the third partial surprised me. I had supposed that the higher partials died out more quickly than the lower, and that the tone which persisted longest was always the first partial. I still suppose that in most bells the first partial lasts the longest, but in the cases of a number of bells to which I have recently listened I find that the third partial becomes very prominent soon after the bell is struck.

Conclusion

The work described in this paper extends our knowledge of the nodal lines of bells, and shows that, although the relative frequencies of the partial tones in the Taylor bells which form the Harkness Chime differ from those of the Meneely bells which form the Dorothea Carlile Chime, nevertheless the nodal lines of both chimes are very similar.

Although the work is not sufficiently accurate to give quantitative values for the relative amplitudes of the different partials, it does seem to show rather definitely that in the bells which have been studied the fifth partial really comes out with surprising strength in the very early stages of the vibration. Just why the fifth partial should be so prominent at first is not entirely clear. It seems to be true however that most of the vibration that gives rise to the fifth partial occurs in the neighborhood of the soundbow. One evidence of this is the fact that the surface of minimum intensity which extends outward from the nodal circle for this partial does not pass directly away from the bell, but runs upward not far from the surface.

Whatever the cause for the early prominence of the fifth partial, the fact that it is at first so prominent supports the suggestion that the strike note is determined by the fifth partial, the octave in which it lies being however misjudged. Another fact which supports this hypothesis is the short time that the strike note lasts. If the proposed hypothesis is correct it would be expected that the strike note should disappear as soon as other partials become as prominent as the fifth. Still another bit of evidence for the hypothesis is a statement by Blessing[4] that if the soundbow of a bell is turned thinner and thinner the strike note decreases in intensity, and that by the time the soundbow is cut off to such an extent that the inner and outer surfaces are parallel the strike note has disappeared. It would be interesting to know what happens to the fifth partial while this process is carried out.

If the above hypothesis is correct, why is the octave so generally misjudged? This question is really one for the psychologist, but in my former paper I hazarded two suggestions, and I may now point out further that the frequencies of the fifth, seventh, and tenth partials—all of which come out strongly from the soundbow—are nearly in the ratio 2:3:4. Now Fletcher[24] has found that when three pure tones with frequencies in the ratio 2:3:4 reach the ear together a note of frequency 1 may also be heard. This would be the frequency required for the strike note, but whether the frequencies of the fifth, seventh, and tenth partials are close enough to the ratio 2:3:4 to produce this effect I am somewhat doubtful.

[24] Harvey Fletcher, Phys. Rev. **23**, 427 (1924).

Against the proposed hypothesis we have Griesbacher's observation[6] that it is possible to get the strike note to respond to a tuning fork. Whether there is some way of reconciling this fact with the hypothesis I do not yet feel sure. The fact that the strike note will not beat with other tones of nearly the same pitch seems incompatible with any actual vibration that has the frequency of the strike note. The best hypothesis that I see at present is that of the misjudged octave.

Before concluding I wish to express my hearty thanks to all who have cooperated in making this study possible: To the Corporation of Yale University, for permission to make use of the Harkness Chime; to the Departments of Physics and Electrical Engineering at Yale University, especially to Professor W. F. G. Swann and Professor H. M. Turner, and to Mr. Enerson and Mr. Pechar, mechanicians at the Sloane Laboratory; to the General Electric Company, especially to Dr. C. W. Hewlett; to the Doolittle Radio Corporation; to the Bell Telephone Laboratories; and to Miss Evelyn H. Puffer, who has carried through a considerable amount of calculation for me.

SMITH COLLEGE,
January 13, 1928.

BOOK REVIEWS

Colloid Symposium Monograph, Vol. V, edited by H. B. WEISER. Pp. 394, numerous figs. Chemical Catalog Company, New York, 1928. $6.50.—This is the fifth volume in this series to monographs in which are published the papers which were presented at the various National Colloid Symposia. The first four symposia were sponsored by the Committee on the Chemistry of Colloids of the National Research Council. This activity has now been assumed by the Colloid Division of the American Chemical Society, and the present volume contains the papers presented at the Symposium held at the University of Michigan in June 1927, with Professor H. R. Kruyt of the University of Utrecht as the guest of honor.

It is the aim of the committee having charge of the program to solicit the outstanding contributions in America for presentation at the symposia, and the reviewer believes that that aim has been consummated. The earlier volumes have contained notable contributions to the theory and practice of colloid chemistry, and the present volume upholds the high standard of its predecessors.

The titles of the various papers indicate clearly the diverse fields in which colloid chemistry plays a rôle, the papers ranging, as they do, from the purely theoretical physical chemistry of interfaces to intensely practical industrial or biological applications. The twenty-four papers noted below are presented in the present volume:

1. Unity in the Theory of Colloids—By H. R. Kruyt.
2. The Stability of Emulsions, Monomolecular and Polymolecular Films, Thickness of the Water Film on Salt Solutions and the Spreading of Liquids—By William D. Harkins.
3. Adsorption and Crystal Form—By Charles H. Saylor.
4. Adsorption from Solution by Ashe-Free Adsorbent Charcoals—By E. J. Miller.
5. Some Unsolved Problems in the Molecular-Kinetic Behaviour of Colloidal Suspensions—By Elmer O. Kraemer.
6. The Measurement of Adhesion Tension, Solid against Liquid—By F. E. Bartell and H. J. Osterhof.
7. Investigations on Molecular Sieve Membranes—By Leonor Michaelis.
8. Synthetic Kidneys—By Wilder D. Bancroft and R. L. Nugent.
9. The Chemistry of Body Processes; The Nature of the Action Between Gelatin and Electrolytes—By A. L. Ferguson.
10. Physico-Chemical Studies on Proteins—III. Proteins and the Lyotropic Series—By Ross A. Gortner, Walter F. Hoffman and Walton B. Sinclair.
11. Relation of Hydrophilic Colloids to Winter Hardiness in Insects—By William Robinson.
12. Colloid Types—By Eugene C. Bingham.
13. The Consistency of Casein glue—By F. L. Browne and Don Brouse.
14. Plasticity and Solvation of Cellulose Esters—By S. E. Sheppard and E. K. Carver and R. C. Houck.
15. A New Rapid Extrusive Type of Plastometer—By Paul N. Geisey and S. Arzoomanian.
16. The Falling Sphere Viscometer and Plasticity Measurements—By H. E. Phipps.
17. The Falling Ball Method for the Measurement of Apparent Viscosity of Nitrocellulose Solutions—By John K. Speicher and G. H. Pfeiffer.
18. The Cellulose Nitrates—By James Craik.
19. The Influence of a Second Liquid upon the Formation of Soap Gels—By Harry N. Holmes and Ralph N. Maxson.
20. Colloids in the Electro-Deposition of Metals—By William Blum.
21. Colloidal Ferric Hydrate in Molding Sand—By George G. Brown and Clyde C. DeWitt.
22. Hydrated Portland Cement as a Colloid—By Alfred H. White.
23. Effect of Electrolytes on Electroendosmose Through Wood Membranes—By Alfred J. Stamm.

24. The Physical Chemistry of Color Lake Formation—By Harry B. Weiser and Everett E. Porter.

It would be a useless attempt to discuss each contribution, for that would extend this review beyond permissible limits. The reviewer believes that the most outstanding papers are those by Kruyt, Harkins, Bartell, Holmes, and Weiser.

Kruyt emphasizes again the fact that the colloid systems are quite different in electrical properties from ionic disperse systems and that a theory which seeks for scientific unity by identifying lyophilic colloids with ionic systems is basically wrong.

Harkins pays particular attention to the nature of interfaces and points out that when interfaces are present, these constitute a new phase and introduce another variable into phase rule studies.

Holmes in a study of gels finds that mere traces of water in some manner favor the formation of gels in a turpentine-sodium stearate system, whereas the reverse effect was observed in a turpentine-sodium oleate system. In the former 0.04 cc of water produced a gel from 0.05 gm sodium stearate and 35.5 cc of turpentine, whereas in the latter 0.03 cc of water destroyed the gelling properties of 0.05 gm sodium oleate and 2 cc of turpentine, whereas in the complete absence of water the sodium oleate would gel with 16 cc of turpentine.

Bartell gives us a practical method for measuring the adhesion tension of a liquid against a solid.

Weiser concludes from his study that color lake formation is due to adsorption reactions and not to the formation of definite salts.

The physical chemist, and the physicist who is interested in the energy relations of interfaces, will find much of interest and of profit in this volume. To those interested primarily in colloids it will be invaluable.

ROSS AIKEN GORTNER

The Properties of Silica. ROBERT B. SOSMAN. 856 pp. American Chemical Society Monograph Series. The Chemical Catalogue Company, Inc., New York, 1927. $12.50. The substance silica presents, in the numerous forms in which it occurs, nearly all of the properties and types of behavior displayed by non-metallic solid substances.

In spite of, or perhaps as the author suggests, because of the inadequacy of our information, it requires over eight hundred pages to present and to critically discuss our present knowledge of the physical properties of this one chemical substance. The so-called chemical properties of silica are not included because, as the author rightly infers, they belong to the subject of the chemistry of silicon. With this restriction of the scope of his subject he has succeeded in presenting in a remarkably clear, complete, and well arranged form the great mass of information which is recorded in a voluminous literature, the result of the labors of some 600 investigators.

The behavior of silica offers many striking illustrations of the fact that, in the present condition of our knowledge, a substance in the solid state can be said to have definite physical properties only in a rather limited sense. That is, complete definiteness in a given physical property attaches not to a given substance in a completely defined state but only to a given sample of the substance in an approximately defined state and at a definite moment. In other words, we have not yet discovered a technic of controlling the variables upon which the properties of a pure solid substance depend which is so perfect as to make these properties independent of the history of the sample. Accuracy of measurement of many properties exceeds our ability to describe the state of the sample in terms which will permit its reproduction.

The present volume is unique in its field and will be found indispensible to any one who has to deal with silica. The information and valuable discussions of principles and measurements which it contains suggest it as a suitable text for use in a graduate seminar.

E. W. WASHBURN

The Rise of Modern Physics. HENRY CREW. Pp. 356, figs. 14. The Williams and Wilkins Company, Baltimore, 1928, $5.00. This book is described in the sub-title as "a popular sketch," and in the preface is said to be "intended for readers who have had but little previous knowledge of the subject, but who would be glad of an informal introduction to this fascinating science."

The book is built around lectures which Professor Crew gave to college juniors and seniors on the History of Science.

Professor Crew has succeeded admirably in his professed purpose. The style is everywhere clear and entertaining, in many places Illumined by flashes of humor. The many personal touches, together with the many excellent photographs introduced in describing the lives and achievements of the men responsible for the advance of physics, not only add to the readableness of the book, but are a most important aid in helping the reader to visualize the conditions under which progress was actually made. Further, Professor Crew often has an illuminating way of stating the points at issue, which may give new ideas to even the professional physicist. His appreciation of Galileo is to be especially commended.

The physicist, whose chief interest in the history of physics is in the better understanding which it gives of the problems now facing us, will regret that no attempt has been made to describe the developments of the twentieth century. It must be said that Professor Crew himself mentions this lack of completeness (on page 341), but nevertheless a history of physics seems strange in which the discovery of the electron is not explicitly described, Einstein is mentioned in only two sentences, and radioactivity is mentioned incidentally in only a single paragraph. The account of spectroscopy is carried further, as one would expect from Professor Crew's special interests.

P. W. BRIDGMAN

Handbuch der Astrophysik, Vol. VI/II. G. EBERHARD, A. KOHLSCHUTTER, H. LUDENDORFF. Pp. 474+ix, Julius Springer, Berlin, 1928. Bound 68.70 R.M. The concluding volume of this important treatise is the first to appear. Like others in the series it is the product of several authors, each dealing with a particular phase of the science. It is worthy of note, as an evidence of the return of the spirit of cooperation in science and a happy augury for the future, that in a volume prepared and edited in Germany one of the invited contributors was an officer of the British army during the great War.

The first chapter, on "The Radial Velocities of the Stars," by Dr. K. G. Malmquist of Lund, is an excellent and impartial statement of what is at present known in this restricted but very interesting field. The various theories of star streaming are clearly discussed, and adequately differentiated from the features upon which they are based.

The second chapter, "Die Verenderlichen Sterne," by Professor H. Ludendorff of Potsdam is worthy of especial commendation. The author, who is recognized as a leading authority in this field, occupies two hundred pages to great advantage, with a clear and comprehensive account of various types of stars which change in brightness. Almost the whole of the space is occupied by an account of the observed phenomena, for the good reason that very little has been done as yet in the way of satisfactory theoretical interpretation. Upon the vexed question of the origin of variation of the Cepheid type, the author passes no judgment. For some other remarkable types of variation, such as R Coronae Borealis, which is usually bright and at irregular intervals becomes very faint, or U Geminorum, which is usually faint, but at intervals becomes twenty times brighter, there is as yet no suggestion of an interpretation.

Not all variable stars are included in this discussion. The novae, or temporary stars, are treated in Chapter 3 by Professor (formerly Colonel) F. J. M. Stratton of Cambridge, who gives an adequate account of the intricate phenomena which they, and especially their spectra, present.

The last chapter on "Double and Multiple Stars," by Dr. F. C. Henroteau of Ottawa, deals with a wide field, including spectroscopic and eclipsing binaries, as well as those observable with the telescope. In the discussion of methods for the calculation of orbits undue prominence is given to certain graphical methods developed by the author, in comparison with others of higher precision.

The treatise as a whole, if it may be judged by this volume, will be of very great value to the serious student of astrophysics, and should be included in the library not merely of all observatories, but of physical laboratories as well.

HENRY NORRIS RUSSELL

Photo-Electric Photometry of Stars (Publications of the Washburn Observatory of the University of Wisconsin, Volume XV.) Part 1. JOEL STEBBINS; Part 2. CHARLES MORSE HUFFER. The appearance of this publication will be welcomed by investigators in stellar photometry, and especially by those who have sought to use the photo-electric cell in such studies. It contains the results of photometric measurements of stars carried on by Stebbins and his associates at Urbana and Madison between 1916 and 1926, together with a description of instruments and methods employed. A pioneer in this exacting field of astronomy Stebbins was fortunate in having the cooperation of Jacob Kunz whose photo-electric cells were used throughout; and he continues to be one of the very few successful operators in this field. The investigations here described are chiefly of spectroscopic binary stars whose orbits are known, so that the times of conjunctions may be predicted. Of the many binaries which were tested, eleven proved to be mutually eclipsing at these times, four or five more are continuously variable in light through the revolution period. An instructive tabulation compares the number of light-variables discovered with the number of binaries tested. Of the binaries having Class B spectra, short periods and very large ranges in radial velocity all that were tested proved to be eclipsing; for others of this class whose velocity ranges exceed 40 km/sec, one-half are variable in light. Of the Class A binaries having ranges greater than 40 km/sec, one-third are variable; but where the range is less, only one in thirty was found to be eclipsing. Complete light curves for seven eclipsing and Cepheid variable stars are discussed in this publication. The high degree of accuracy here attained excites admiration for the apparatus and especially for the observers. Those who have worked with the photo-electric photometer will fully appreciate Stebbins' word of warning, that it is a temperamental instrument requiring considerable patience for its successful operation.

ROBERT H. BAKER

Physikalisch-Chemische Uebungen, Vierte Auflage. W. A. ROTH. Pp. 316+VIII, 71 figs. Leopold Voss, Leipzig, 1928. Bound 15 R.M. It will be sufficient to call attention to the new edition of this excellent work which includes exercises in the various fields of physical chemistry, not excepting colloid chemistry. It will be a valuable source of instructive experiments to any teacher who may desire for any reason to supplement his chosen laboratory manual. Not the least useful feature of Dr. Roth's book is due to the fact that the description of the laboratory technique is accompanied by an exposition of the theory underlying the experiment.

F. H. MACDOUGALL

Elementary Physical Chemistry. HUGH S. TAYLOR. Pp. 531+VII, 107 figs. D. Van Nostrand Co., New York, 1927. This volume is an adaptation of the two-volume "Treatise of Physical Chemistry" which appeared three or four years ago under the author's editorship and was very warmly received. The author undertakes to present at this time material suitable for an introductory course. The scope and arrangement will be clear from the following list of subjects treated: The Atomic Concept of Matter, Energy in Chemical Systems, States of Aggregation (Three Chapters), Velocity and Mechanism of Gaseous Reactions, Direction of Chemical Change, Solutions, Homogeneous Equilibria, Heterogeneous Equilibria, Conductance and Ionization, Ionic Equilibrium (Weak Electrolytes, Strong Electrolytes), Photochemistry and Colloid Chemistry.

The book must be characterized as a successful attempt to describe in moderate compass the fields of physical chemistry which are at present of chief interest and importance. The author is to be commended for his insistence on a knowledge of the Calculus as a prerequisite to any serious endeavor to master modern physical chemistry. In general, the treatment is quite adequate. Exception must be taken, however, to the following definition of viscosity (page 124): "Viscosity may be defined as the force in dynes necessary to move a square centimeter of liquid surface past a stationary liquid surface one centimeter distant."

F. H. MACDOUGALL

To the Editor of the Physical Review.—In your March issue you were kind enough to publish a review of my book, "The Evolution of Scientific Thought." May I be permitted the liberty

of calling your attention to a slight inaccuracy of interpretation on the part of the reviewer (P. W. Bridgman).

I am criticised for having upheld a "meaningless" point of view on the subject of the objectification of Newton's absolute space and of Einstein's space-time of the special theory. In this connection I would like to say that the "point of view" in question is Einstein's; he insists on it repeatedly, stressing it as one of the contributing motives that prompted him to generalise his special theory. I endeavored to make this clear by giving quotations from Einstein's own writings on the matter (e.g. pages 330, 462 and 466 of my book). Although I heartily agree with Einstein's stand, I am not the originator of his views and I feel that the reviewer has misinterpreted the spirit of my book by presenting them as belonging to me personally and criticising me on this basis.

The reviewer also objects to my having denied the influence of Newton's theological ideas on his scientific discoveries; the criticism being made that I have thereby proceeded "without examination of the historical facts." It is true that I have not echoed Mr. Burtt's ideas as expressed in a recent book to which Professor Bridgman directs me for historical accuracy. On the contrary, I have obtained my information from Newton's own writings and from the works of recognised scientific authorities who have dealt with the matter. None of them have ever found it necessary to hint that Newton had allowed his theology to run away with his science. Mach notably, who has never been accused of historical inaccuracy and who was Newton's keenest critic, took the same stand as I have taken when he wrote: "Newton never, despite his profound religiosity, mingled theology with the questions of science." (The Science of Mechanics, page 457—Open Court Publishing Co.)

A. D'ABRO

PROCEEDINGS

OF THE

AMERICAN PHYSICAL SOCIETY

MINUTES OF THE WASHINGTON MEETING, APRIL 20–21, 1928

The 151st regular meeting of the American Physical Society was held at the National Academy of Sciences in Washington, D. C., on Friday and Saturday, April 20 and 21, 1928. The presiding officers were Professor Karl T. Compton, President of the Society, and Professor Henry G. Gale, Vice-President of the Society.

On Friday evening there was a dinner for the members of the Society and their friends at the Hotel Raleigh. The speakers at this dinner were Professor J. Franck, Professor L. Brillouin, Dr. Herbert E. Ives, and Sir Richard Paget.

At the regular meeting of the Council held on Friday, April 20, 1928, one was elected to fellowship, eight were transferred from membership to fellowship and thirty were elected to membership. *Elected to Felloswhip:* R. J. Lang. *Transferred from Membership to Fellowship:* R. M. Bozorth, J. B. Johnson, A. L. Kimball, H. C. Urey, M. S. Vallarta, E. C. Watson, R. L. Wegel, and E. C. Wente. *Elected to Membership:* R. E. Badgley, S. W. Barnes, C. M. Blackburn, W. Bleakney, C. Boukner, J. G. Brainerd, H. C. Burbridge, A. F. Daniel, O. R. Ford, S. F. Gaddes, M. C. Holmes, P. A. Johnson, Jr., D. Kirkpatrick, C. A. Kotterman, E. S. Lamar, W. N. Lowry, E. R. Mann, K. J. Miller, N. M. Mohler, D. W. Mueller, I. O. Myers, R. D. Potter, R. H. Ranger, V. Rojansky, E. E. Smith, P. L. Spencer, J. E. Thompson, R. R. Tileston, M. W. Trawick, R. K. Waring.

The regular program of the American Physical Society consisted of 109 papers, numbers 8, 12, 31, 34, 40, 46, 70, 73, 77, 86, 90, 93, 94, 96, 100, 103, 104, 105, 106, 107, 108, and 109 being read by title. The abstracts of these papers are given in the following pages. An AUTHOR INDEX will be found at the end.

HAROLD W. WEBB, *Secretary*

ABSTRACTS

1. Some photographs of optical images after Abbe. R. A. WETZEL AND GEORGE NEEDHAM. College of the City of New York.—The new Pulfrich-Abbe demonstration microscope is rich in interference and diffraction phenomena. A camera attached to the visual system gave permanent records of many interesting images; for example: two different objects may be made to look alike by choosing the conditions of coherence. For "objects" we have used gratings with the following rulings per millimeter: one plane, 15; two reciprocal, 5; two displaced $\frac{1}{2}\delta$, 3; two crossed at 90 degrees, 7; three crossed at 60 degrees, 6. An interesting diffraction effect simulates spectroscopic self-reversal; another, absorption spectra.

2. The continuous spectrum of mercury. L. H. DAWSON AND W. H. CREW, Naval Research Laboratory, Washington, D. C.—Intensity maxima of the bands of continuous radiation from a mercury arc coincide with the spectral series limits; this is in agreement with the theory (Bohr, Wright, and others) that the continuous spectrum is due to electrons with various kinetic energies plunging into the outer orbits associated with spectral series. Band maxima observed in an arc at atmospheric pressure, excited by high voltage, low current discharge are: (associated series limits are given in brackets): λ4500[λ4580]; λ3300[λ3300]; λ2350[λλ2490; 2230; 2140]. Under these conditions no continuous radiation is emitted in the region λ2535–λ2350 corresponding to the limit λ2490. However, upon increasing the current through the arc, the bands broaden in both directions and fill up this gap; furthermore, the broadening of λ2536 and lines of the diffuse series give a fairly even distribution of continuous radiation throughout the entire spectrum. In passing from a high current to a low current arc certain lines rapidly decrease in relative intensity, which shows that the latter condition of excitation is unfavorable for electron transitions into the 2^3P-levels, a fact consistent with the non-appearance of a band at λ2490.

3. Intensities of the lines of the mercury spectrum. E. O. HULBURT, Naval Research Laboratory, Washington, D. C.—The total radiation, measured with a thermocouple, in all directions in the spectral region λ600 to 230$\mu\mu$ from a small quartz mercury lamp of known size filled with mercury vapor at atmospheric pressure was 1.54×10^5 erg sec^{-1}. Assuming all the light to be in quanta of λ500$\mu\mu$, this gave about 50 quanta emitted per atom per second. The intensities of the lines of the spectrum were measured with a quartz spectrograph, a thermocouple and a photo-electric cell, all calibrated, and in some cases with a photographic densitometer. Plotting the logarithm of the intensity against the frequency for the lines of a series gave roughly straight lines of about the same slope for the sharp series ($2^3P_n - m^3S_1$) and for the diffuse series ($2^3P_n - m^3D_{123}$). The temperatures of the excited atoms derived from the slopes, on simple theory, were of order 10^3 degrees, which seemed reasonable.

4. The absorption spectra of mixtures of mercury and thallium vapors. R. K. WARING' Johns Hopkins University (Introduced by R. W. Wood).—In the absorption spectra of mixtures of mercury and thallium vapors certain bands have been photographed which have not been observed in the spectra of either metal alone. It is thought that the origin of these bands is a mercury-thallium molecule. Most of the bands are sharp on the side of shorter wave-lengths, and shaded toward the longer wave-lengths, broadening more toward the long wave-lengths than the short when the temperature is increased. The region investigated extends from about 2200A to about 7000A. The vapors were studied at temperatures ranging from 300°C to 1100°C. In no case has the resolving power been sufficient to show the fine structure. The results confirm an early experiment on the subject (Wood and Guthrie, Astrophys. Jour. 29, 211(1909). Contributary evidence in favor of a mercury-thallium molecule resulted from an experiment which indicated that the amount of thallium which was vaporized in a closed tube at 600°C was greatly increased by the presence of mercury vapor.

5. Optical excitation of mercury and the sensitized fluorescence of mercury-hydride, OH, ammonia and other compounds. R. W. WOOD AND E. GAVIOLA, Johns Hopkins University.—The reactions occurring in a quartz tube containing mercury vapor, in the presence of other gases when illuminated by the light of the water cooled quartz mercury arc have been studied. Band spectra appear together with the optically excited arc lines of mercury. Some of these bands have been identified with the bands of mercury hydride, OH and ammonia which have been studied by other observers. By employing a wire gauze as absorbing screen placed first between the lamp and the resonance tube, and then between the resonance tube and the spectrograph it is possible to determine whether a given line or band results from a single or two two stage absorption processes. An exhaustive study of the effects of other gases on the intensity ratios of the optically excited mercury lines has also been made.

6. Intensity variation at critical points in the helium spectrum. I. CORNOG, J. T. LAY AND C. B. BAZZONI, University of Pennsylvania.—Photographs of the helium spectrum produced in an equipotential space from an equipotential cathode have been studied photometrically in

order to determine the variation in line intensities on passing the various critical potentials. The results here reported on cover the 54 volt point at which double ionization is first possible. Spectra were taken at intervals of 0.2 volt at suitable values between 50 and 60 volts. The plates show a marked minimum of intensity near 54 volts generally for all lines but interesting variations in rate of change of intensity in the different series are recorded. A photometer using a vacuum thermopile was developed for use in this work.

7. Ionizing potentials of light atoms. LOUIS A. TURNER, Princeton University.—Millikan and Bowen's Moseley curves for ionizing potentials of light atoms are extended by adding points for Ne^+ and Na^+, and improved in regularity by amending their tentative values for F and F^+ from 16.9 and 32.3 volts to 17.4 and 34.4 volts, on the basis of consideration of the energies of removal of ($3s$) electrons from these excited atoms and ions. The energy for removal of a $2s$ electron can be computed from Bowen's data by adding to the ordinary ionizing potential the energy corresponding to the appropriate a-b line of the next spark spectrum. Absorption of this line after ionization raises an electron from the $2s$ to the $2p$ group filling the vacancy in the latter, leaving the atom as if a $2s$ electron had been removed directly. Moseley lines for these energies, the L_{II} energies, have somewhat smaller slopes than those of the corresponding $2p$ lines but nearly the same as is, of course, implied by the fact that the a-b lines follow the irregular doublet law. Extrapolations suggest that the 320.9 and 323.2 lines of Mg correspond to $(2s)(2p)^6(3s)^2 \rightarrow (2s)^2(2p)^5(3s)^2$ transitions and the 231.4 line to $(2s)^2(2p)^5(3s)^2 \rightarrow (2s)^2(2p)^6(3s)$ or $(2s)^2(2p)^5(3s) \rightarrow (2s)^2(2p)^6$ transitions.

8. Ionization potential of hydrogen atoms from the viewpoint of the electromagnetic quantum theory and polarization of light from canal rays. CORNELIO L. SAGUI, Castelnuovo dei Sabbioni, Arezzo, Italy.—The structure of a hydrogen atom, from the viewpoint of this theory, seems to result from the assembly of about 1800 electrons distributed in 60 energy levels in which the density of the electrons is proportional to the energy of each level. Such a density would consequently decrease from the center of the atom to its surface. The electrons of the energy-level $R((1/3)^2-(1/4)^2)$ would be those more easily ejected by impact of bombarding electrons, and 13.78 volts was in this case the ionization potential found. Polarization of light from canal rays was supposed due to a component of the oscillating electrons parallel to the motion of the hydrogen atoms. It is also shown that the polarization would not be uniform but would result in a sort of wave.

9. The nature of the production of one of the spark lines of mercury and the determination of the mean life. L. R. MAXWELL, National Research Fellow, Bartol Research Foundation.—In a paper presented to this Society recently the author described a method for obtaining spark lines due to Hg^{++}. These lines showed a displacement in the direction of the crossed-electric field. The variation of intensity of one of the lines (4797A) has now been measured for different positive ion currents and found to be the same for all points along the line and approximately proportional to the ion current. This shows, on calculating how the intensity should vary, that the line is the result of a single electron collision with the neutral atom. Line intensity measurements obtained as a function of the position across the beam show that when the ion is put into the excited state it will then radiate according to the probability law, and that the mean life is of the order of 10^{-7} sec.

10. An optical study of adsorbed films. K. HERZFELD AND J. H. FRAZER, Johns Hopkins University.—Rayleigh's and Drude's method which makes use of the ellipticity of light reflected from a surface covered with a thin layer, has been recently applied to the study of adsorption. This method was improved by using a Point-o-lite lamp as a source, and by measuring the light intensity photometrically instead of compensating the ellipticity with a Babinet compensator. Only one Nicol is necessary with this method. It is possible to detect a layer of about 1A on a surface of 5 sq. mm. With less accuracy a surface of 1/20 sq. mm is sufficient. The adsorption of water vapor and of other vapors on glass has been studied. In agreement with previous measurements by Langmuir and Frazer and Patrick, there is no adsorption of water vapor up to 1 mm. Then a layer of less than 1 molecule thickness goes up to the satura-

tion point at 21 mm. The method has furthermore been applied to transition layers between glass and liquids. It can be used to study the corrosion of the glass and the adsorption of dissolved substances on the glass surface.

11. Spreading of illumination beyond the edge of an image. LUDWIK SILBERSTEIN, Kodak Research Laboratories, Rochester, N. Y.—This paper contains a theoretical investigation of the spreading of scattered light in a plane layer of turbid medium. A semi-plane bounded by a straight edge being assumed to be directly exposed to collimated light, a formula is derived for the scattered light flux as a function of the depth and the distance from the edge of the illuminated area.

12. The distribution on a surface of evaporating parallel wires for producing uniform metallic films. OTTO STUHLMAN AND E. R. MANN, University of North Carolina.—A theoretical discussion of the distribution on a concave surface of a small number of evaporating parallel wires, whose condensed metallic vapour can produce, upon a plane located at some distance below, a plane metallic film of any desired thickness. For a single wire placed at a height h above and parallel to the condensing plane, the thickness $t=mh/2\pi(h^2+x^2)$, where m is the mass evaporated per second per unit length of wire and x the distance in the plane of condensation, measured on either side of the wire. Theoretically the necessary conditions for uniform thickness are an infinite number of parallel wires placed infinitely close together in a plane parallel to the condensing plane. The best experimental approximation obtained by five wires is a distribution forming a cylindrical surface. A specific case experimentally under consideration is: positions of wires with respect to the condensing plane are $(-5, 5)$, $(-1.34, 8.66)$, $(0, 10)$, $(1.34, 8.66)$, $(5, 5)$ producing a film of uniform thickness having a width of 8 cm and any desired length. The thickness is expected not to exceed 2% in error at the edge.

13. A relation between thermal conductivity, specific heat and absolute temperature. C. C. BIDWELL, Lehigh University.—A study of recently obtained data on thermal conductivity and specific heat of lithium, sodium and zinc over the temperature range -250°C to $+200$°C reveals a simple relation between these quantities not hitherto reported, namely the law, $k/s=K/T+K'$. k is the thermal conductivity; s, the specific heat; T, the absolute temperature; K and K', constants. The values of k/s, when plotted against $1/T$ fit a straight line with remarkable precision. In the case of lithium the line goes through the origin. For sodium $K'=0.6$, for zinc $K'=2.0$. The law holds down to -200°C for lithium, below which the abnormal increase in k causes a deviation; to -225°C for zinc below which a deviation is noticeable. For sodium there is no deviation from the law even as low as -240°C the lowest temperature at which we have data. Considering the thermal conductivity of a metal as made up of two parts, transfer of energy by atomic collisions and by elastic waves along an ionic lattice we have $k=(\rho v'\lambda' s/4)+(\rho v\lambda s/3)$. The first term on the right refers to the ionic lattice (Debye). v' is the velocity of sound in the lattice. λ' is a dissipation factor and refers to the distance in which the energy of the wave is reduced to $(1/e)$th part. Assuming λ' inversely proportional to the temperature we get the law above.

14. Thermal and electrical conductivity of single and poly crystal zinc. E. J. LEWIS AND C. C. BIDWELL, Cornell University.—Thermal conductivity measurements over the range -250°C to $+100$°C were made on rods of single and poly crystal zinc using a modification of the Forbes bar method previously used by Bidwell on rods of sodium and lithium and described by him. The single crystal rod was prepared in vacuum by Bridgman's method. One of the poly-crystal rods, rod No. 1 was cast in the open air; the other, rod No. 2, in vacuum to avoid oxide contamination. The thermal conduction was found to decrease smoothly but not linearly with rise of temperature. The single crystal zinc shows 11% better thermal conductivity at 0°C than the poly crystal zinc No. 2 and about 18% better than No. 1. In the case of the single crystal rod the conductivity was measured in the direction of the basal or cleavage planes which are parallel to the axis of the cylinder. The density of the atoms is said to be greatest in these planes. The single crystal rod showed about 20% less electrical resistivity at 0°C than the poly crystal rod No. 2, and about 30% less than No. 1. The Wiedemann-Franz-Lorenz ratio

k/CT rises to a maximum at about -100°C, decreasing slightly at higher temperatures ultimately reaching for the single crystal rod the value 24.7×10^{7}, the value the simple theory requires as a constant.

15. A generalized Gibbs Boltzmann equation. F. RUSSELL BICHOWSKY, Naval Research Laboratory, Washington, D. C.—A generalized form of the Gibbs Boltzmann canonical equation $1=\int\phi(\epsilon/\kappa T)e^{-(\alpha+\epsilon)/\kappa T}d\omega$ is derived by reversing the line of proof used by Gibbs in showing the correspondence of statistical formula with thermodynamics. The proof involves only the assumption of the first two laws of thermodynamics, the idea that thermodynamic quantities are the physical average of complicated molecular processes, and the assumption that energy entropy and temperature give a sufficient description of the system considered. The equation allows a treatment of statistics of the most generalized type of systems.

16. A method for the precise determination of thermal capacities. T. E. STERN, Princeton University. (Introduced by K. T. Compton.)—It was found that a modified Bunsen ice calorimeter was capable of yielding very consistent values for the total heats of substances at temperatures between 0° and 440°C. The substance under investigation was contained in a metal capsule, by the use of which errors due to cooling and radiation during the fall of the specimen into the calorimeter were largely eliminated. Thermal contact was established in the calorimeter by the use of a metal cup surrounded by water and containing mercury. Results were obtained directly in terms of the mean calory, since the heats liberated were compared with the heat given out by a capsule containing water. From the total heat equations the specific heats were readily obtained. The probable error of a single observation was, on the average, 1 part in 1000; for quantities of heat of the order of 240 calories. The probable errors of the total heat values were also 1 in 1000.

17. An improved arrangement for obtaining high speeds of rotation. ERNEST O. LAWRENCE, J. W. BEAMS, AND W. D. GARMAN, Yale University.—Henriot and Huguenard (Jour. d. Phys. et Ra., **8**, 443 (1927)) have described a method whereby high rotational speeds are obtained. Instead of usual mechanical bearings with oil lubrication, the rotating body rides on a whirling jet of air. In making use of this method we have found that an essential condition for satisfactory performance is the elimination of vibrations in the nozzle from which the compressed air jet issues. The "rotor" is separated from the nozzle by an air film of small thickness so that if vibrations of sufficient amplitude develop the rotor and nozzle come into direct contact. A rubber mounting for the nozzle is described which damps out such vibrations and permits steady speeds of rotation for a rotor 16 mm in diameter of between 5000 and 6000 revolutions per second.

18. Differential intensity sensitivity of the ear. R. R. RIESZ, Bell Telephone Laboratories, Inc.—The minimum perceptible increment in the sound intensity of a pure tone was measured as a function of frequency and intensity over practically the entire range of auditory sensation. The data are presented as the ratio of minimum perceptible increment in intensity to total intensity; i.e., $\Delta E/E$, which ratio has been called differential sensitivity by N. E. Dorsey. Measurements were made by impressing known alternating e.m.f.'s from two vacuum tube oscillators into the circuit of a special telephone receiver, the values of the e.m.f.'s being capable of independent adjustment. The most consistent results were obtained by keeping the frequencies of the two oscillators different by 3 c.p.s. An observer was unable to detect the two tones as such but heard a single tone whose intensity was beating or fluctuating three times per second. One e.m.f. was held at a known multiple of the threshold value and the other e.m.f. varied until the observer was unable to detect the fluctuation and the value of $\Delta E/E$ calculated from the e.m.f.'s. Measurements were made at frequencies of 35, 70, 200, 1000, 4000, 7000 and 10000 c.p.s. and at intensities from the threshold of hearing to the threshold of feeling. At any frequency $\Delta E/E$ is constant for intensities greater than 10^{6} times the threshold intensity but increases as the intensity is decreased below this value. Above this intensity Weber's law ($\Delta E/E=$constant) holds. As a function of frequency $\Delta E/E$ is a minimum at about 2500 c.p.s. Curves are given and empirical relationships between differential sensitivity, frequency and intensity derived.

19. An experimental determination of the relation between viscosity and frequency in vibrating solids. S. L. QUIMBY, Columbia University.—A bar of the material under examination with a small iron armature attached to each end is suspended by light silk fishline. Opposite one armature is placed the magnet of a telephone receiver and opposite the other an electromagnet which is connected to a source of variable frequency alternating current. The bar is excited to resonance at one of its harmonics and while in this condition the excitation is suddenly removed. The amplitude of vibration diminishes exponentially at a rate which depends upon the frequency and the viscosity of the material. The e.m.f. induced in the telephone receiver, which is proportional to the amplitude, is rectified, amplified, and photographed on an oscillograph giving a record from which the decrement of the vibrations and the viscosity may be obtained. Experiments were made over a frequency range of 500 to 3000 cycles. The results are in agreement with those obtained by Kimball below 200 cycles and permit the generalization of his conclusion that in solid media the fractional loss of energy per cycle due to internal friction is a constant of the material independent of the speed of performance of the cycle.

20. Some experiments with a vibrating quartz sphere. K. S. VAN DYKE, Wesleyan University.—The rotation which a vibrating piezo-electric quartz plate may perform is well known and has been attributed by Meissner to an air blast from the vibrating plate. The present author finds that a vibrating quartz sphere may perform either translational or rotational motions. Strong winds are sometimes found near the sphere which, undoubtedly, play a part in determining its motion. However, as the mechanical driving forces persist at pressures so low that the wind is thought ineffective, the ponderomotive effects, and presumably the air blasts as well, seem to be due to a sort of grip that the quartz has upon its support. This grip if greater at some parts of the vibration cycle than at others could account for the forces operating. The sphere can be made to slide along a track without rolling, to travel continuously around a circular track in either direction or to rotate continuously about an axis which it selects. Some notion of the character of the motion of the various parts of the surface of the sphere is obtained from the rotation which ping-pong balls take up when allowed to touch the apparently still, but vibrating, sphere.

21. Discussion of the kinetic theory of gravitation IV: Correlation of continual generation of heat in some substances, and impairment of their gravitational acceleration. CHARLES F. BRUSH, Cleveland, Ohio.—Long and careful search with sensitive calorimeters has discovered some substances, notably complex silicates, which remain permanently warmer than their surroundings. This continual generation of heat is thought due to ether-waves causing gravitation. (There is no appreciable radioactivity.) Conversion into heat of some of the energy of the ether-waves, however little, might be expected to impair to some extent the falling velocity of a heat-generating substance; *and all such substances thus far tested have clearly shown impairment.* Two aluminum containers are used, alike in size, shape, weight and smoothness of surface. These are dropped simultaneously, side by side, by sudden removal downward and sideward of the supporting horizontal metal plate. After falling about 110 cm, the small lower ends of the containers are photographed against a white background having many horizontal black lines, and illuminated by a bright electric spark. One container is filled with the silicates under test, while the other is loaded with an equal weight of lead sawdust. Eight photographs are made on successive strips of the same plate, the containers being reversed in right and left position after each exposure. The photographs easily show that the container holding the silicates is consistently slow. Exchange of loads in the containers makes no observable difference—the silicate container is always slow.

22. An active form of oxygen. L. C. COPELAND, Johns Hopkins University. (Introduced by F. R. Bichowsky.)—An active form of oxygen presumably monatomic has been produced by passing oxygen gas saturated with water vapor through a discharge tube. Density measurements indicate a dissociated gas and association to a heavier molecule, such as O_3. Platinum and nickel wires are heated to glowing in this gas and copper and tungsten are apparently unaffected. Luminescence is produced by mixing iodine vapor or sulphur vapor with the active gas.

23. Atomic absorption coefficients. R. M. LANGER, National Research Fellow, Bureau of Standards.—It is difficult to check calculations of intensity of emission for atoms because the conditions of excitation can not easily be analyzed. Absorption measurements are more easily interpreted and it is interesting to calculate these by the new mechanics and try to compare with experiment. The theoretical values are surprisingly high. For example, the atomic absorption coefficient of normal hydrogen atoms for the first lines of the Lyman series are respectively 37, 7.0, 2.4, 1.2, 0.7, all multiplied by 10^{-4}. Correspondingly for the Balmer series (i.e., atoms in the first excited state), one finds 40, 13.5, 8.0, 6.0, 4.5, 4.0, all multiplied by 10^{-3}. These are presumably for radiation which differs from the absorption frequency of the particular atom by less than the natural line width. The apparent absorption coefficient will of course depend on the Doppler width and on the resolving power of the observing apparatus and will be much smaller than the values here given.

24. Investigation of materials useful in the construction of filters for the ultra-violet. CHARLES D. HODGMAN, Case School of Applied Science.—Gelatin film, ordinarily used in filters for the visible spectrum, may be employed where transmission is not required for wave-lengths shorter than 0.30μ. Films of celluloid or collodion transmit very little below 0.32μ and it is less convenient to incorporate the absorbing agent. Cellophane film readily absorbs dyes from aqueous solutions and has a considerably higher transmission than gelatin in the shorter wave lengths. Measures of the transmission of equal thicknesses (0.005 cm) of gelatin and of cellophane made by the sector photometer show the values to be approximately as follows:

Wave-length, microns	0.20	.25	.30	.35	.40
Percent transmission of Gelatin	0	7	35	58	70
Percent transmission of Cellophane	16	30	47	65	78

Alteration of the transmission due to continued exposure to the ultra-violet is being investigated. Preliminary measures for gelatin and cellophane in which the materials were exposed to the radiation from a quartz mercury-vapor arc at a distance of 25 cm for a period of 12 hours indicate no measurable change. The transmission has also been determined for a large number of other materials which may be of use in filter construction.

25. On the distribution of ionic mobilities in air. JOHN ZELENY, Yale University.—The author's blast method of measuring ionic mobilities in gases has been modified to permit a determination of the distribution of the mobilities, which are found to cover a wide range of values. Gas is passed between the two electrodes of a cylindrical condenser, a narrow section of the inner of which is connected to an electrometer. Ions are introduced into the gas stream from the outside through small holes in the outer cylinder and the distance measured that they are carried downstream while they move from the outer to the inner cylinder under an electric field. The method has a high resolving power. Preliminary measurements made on ions over 3 seconds old, in filtered air containing about 4 mg of water per liter show a broad band of mobilities both for negative and positive ions, the positive band being somewhat broader than the negative. The highest mobilities in these bands are about 2.5 times as fast as the lowest. The most numerous ions were found to have mobilities of approximately 2.2 and 1.3 cm/sec. for the negative and positive ions respectively. The results are in agreement with the recent work of Laporte.

26. Gas ion mobilities in H_2–SO_2 mixtures. L. DU SAULT AND LEONARD B. LOEB, University of California.—Apparently two states of purity of SO_2 exist after careful fractionation whose appearance cannot be controlled. In the one the mobility at N. T. P. on the accepted scale is 0.28 cm/sec per volt/cm for positive ions and 0.26 for negative ions. In the purer sample the values are 0.40 cm/sec and 0.37 cm/sec. At lower pressures the reduced mobility apparently increases to 0.30 cm/sec and 0.28 cm/sec respectively. This is probably due to the purer sample predominating at these pressures. In mixtures with H_2 both samples give a mobility mixture curve for negative ions departing from Blanc's law as does NH_3. The lower mobility gas shows an identical effect with the positive ions. The purer gas *increases* the mobility of

the *positive ion* in H_2 to *as high as twice the normal observed negative* mobility. Similar increases were observed on traces of NH_3 in H_2 but the increase was not so large. The curve in this case cannot be followed to higher percentages as the pure modification was obtained but once at higher pressures. As neither + nor − ions in H_2 are formed about an H_2 molecule this indicates that the SO_2 replaces some more bulky constituent and makes a more mobile ion. Contrary to Yen, the + mobility was universally higher than the −.

27. The nature of gaseous ions from a study of mobilities in mixtures. LEONARD B. LOEB, University of California.—After a general survey of the previous status of the question of the nature of the gaseous ion, it is concluded that for pure gases the dielectric attraction of the molecules by the charged ion can account for the order of magnitude of the mobility nearly equally well on either cluster or small ion theory. Such measurements are therefore indecisive. The measurements of mobilities in mixtures use Blanc's law as a criterion for the absence of the change of the cluster ion. The results show that Blanc's law holds in some cases and not in others. The observed nature of the mobility curves in mixtures shows three types of effects. These may be interpreted as indicating absence of clustering, labile clustering, stable clustering. The nature of the deviations in different gases indicates that where marked stable clustering occurs it is a specific effect depending on the chemical nature of the gas and sign of charge on the ion. Such effects are superimposed on the dielectric attractions mentioned above. Erikson's results on aging are discussed in their bearing on this work.

28. A proposed experiment on the statistical interpretation of quantum mechanics. ARTHUR EDWARD RUARK, Mellon Institute, University of Pittsburgh and Gulf Production Companies.—Consider the wave function $\Psi = \Sigma c_n \Psi_n$, where Ψ_n is the characteristic function of the nth quantum state. According to one view $c_n c_n^*$ measures the fraction of the systems of a statistical ensemble in the nth quantum state. Another view is that $c_n c_n^*$ measures the strength of excitation of the nth mode of vibration in each atom. If several modes of vibration can exist simultaneously in a single atom, then probably several quanta can be emitted at the same time. This could be tested for nuclear-spectra with a Rutherford-Andrade gamma-ray spectrograph. Instead of a photographic plate, small point counters would be so placed that each one receives diffracted gamma-rays of a definite wave length. The existence of double emissions from one and the same nucleus can thus be tested. The counting experiments of Kovarik (Phys. Rev. **23,** 599 (1924)) indicate that only one gamma-ray is emitted by each decomposing atom of RaB or RaC. The experiment of Compton and Simon (Phys. Rev. **26,** 290 (1925)) also speaks against the existence of double emissions, which would require that the law of conservation of energy should have only statistical validity.

29. Rotational Distortion and Zeeman Effect of Diatomic Molecules in Wave Mechanics. CLARENCE ZENER, Harvard University.—The condition that Pauli's equations $(H_0+H_1-E)\psi_\alpha=0$, $(H_0+H_1+E)\psi_\beta=0$ be soluble is that the determinant $|H_0+H_1-E|$ vanish. In rotational distortion and Zeeman effect, $H_1=A(\sigma_k\cdot s)$, $H_1=A(\sigma_k\cdot s)+(\sigma_k\cdot H)+2(s\cdot H)$ resp. The solution of this determinant gives to the first approximation in the power series of A:

$$\Delta E = \pm\sigma_k^2 As/(j+\tfrac{1}{2}\pm s)+\sigma_k^2 As/2(j\pm s)(j+1\pm s)$$

$$\Delta E = \{-(m+\tfrac{1}{2})\sigma_k^2 H+\tfrac{1}{2}\sigma_k^2 As\}/(j\pm s)(j+1\pm s)$$
$$\pm[4s^2H^2+\{2\sigma_k^2 sH^2-4(m+\tfrac{1}{2})\sigma_k^2 s^2 AH+\sigma_k^4 s^2 A\}/(j\pm s)(j+1\pm s)$$
$$+\{\tfrac{1}{4}\sigma_k^4 H^2-(m+\tfrac{1}{2})\sigma_k^2 SAH\}/(j\pm s)^2(j+1\pm s)^2]^{1/2}$$

The rotational distortion separation is in agreement with Kemble's and Van Vleck's formulae only for large values of j. The second term gives the anomaly when $j=\sigma_k\mp s$. The second formula gives the coupling between the Zeeman effect and multiplet structure.

30. An attempt to detect a magnetic field resulting from the rapid rotation of a copper sphere. W. F. G. SWANN AND A. LONGACRE, Bartol Research Foundation of Franklin Inst.—In an explanation of the earth's magnetism as a result of rotation, the apparent current density i must be considered as a function of the density D, angular velocity ω, and distance r from the

axis of rotation. Confining ourselves to forms of i involving only products of simple powers of r and ω, there are two expressions which would be consistent with the ratio of the earth's magnetic field to that of the sun, and with a reasonably small value for the field of a small sphere rotating at high speed. These expressions are: $i = ADr\omega$, and $i = BDr^3\omega^4$. As corresponding to the field of 0.5 gauss at the earth's pole, the former predicts 3.2×10^{-9} gauss and the latter 4.4×10^{-3} gauss for the magnetic field at a pole of a copper sphere 10 cm in radius rotating 200 times per second; observations made on such a sphere using a compensated earth inductor compass, and with the earth's field balanced by Helmholtz coils, gave measurements corresponding to a field at the pole of less than 7.0×10^{-4}. The experiment, while favoring the first of the above expressions for i does not form conclusive evidence against the second for bodies and sizes and angular velocities comparable with those of the earth and sun. Thus for example a law which made i proportional to $\omega^{3.8}$ would give practically the same ratio for the fields of the earth and the sun as would the fourth power law. For the high speed sphere, however, this expression would give a negligibly small field.

31. The rotation of permalloy and soft iron by magnetization in weak fields and the gyromagnetic anomaly. S. J. BARNETT, University of California at Los Angeles and California Institute of Technology.—This is an extension of the work presented at the June meeting, 1927 (Phys. Rev. **30,** 964 (1927)). Many additional measurements with the magnetizing solenoid wound upon the rotor have been made under improved conditions; also many with the solenoid fixed to the earth, as in most earlier work by others. The method used in the principal part of the investigation is essentially a null method, though two deflection methods have also been used. All are alternating current methods, involving the use of resonance and rectangular waves. The results of all are in excellent agreement. The mean (preliminary) value of ρ (ratio of angular momentum of elementary magnet to its magnetic moment) obtained is $m/e \times 1.05+$, which agrees closely with the value $(m/e \times 1.06)$ obtained in the precise work on magnetization by rotation published in 1925. Systematic errors have been thoroughly studied. The total error is probably less than one percent. The magnetizing fields used in all the work have been weak, the intensities ranging approximately from 20 to 40 gausses. Rotor diameters have ranged from 1.5 mm to 3.2 mm; frequencies from 4.1 per second to 13.9 per second; and amplitudes of vibration (when not reduced to smaller magnitudes in the practise of the null method) from 4 cm to 16+ cm. The magnetic parts of all rotors are either 20 cm or 27.5 cm in length.

32. The Hall effect in single iron crystals. P. I. WOLD, Union College.—Silicon steel, with about 3.8 percent silicon, has been obtained in the form of long single crystals about 1.5 cm wide and .3 cm thick. The crystal orientation is different for the various specimens. In some cases about half the specimen is monocrystalline and the remainder polycrystalline. The Hall effect has been measured on several of these and in various places. The Hall constant appears to be independent of the direction of orientation of the large crystals and does not differ substantially from that obtained in the polycrystalline portion. The results are in agreement with those obtained with single crystals of copper and it is believed that this is what should be expected for a metal of cubic lattice structure. The values obtained for the Hall effect in this silicon steel are about 15 times greater than for pure iron.

33. An x-ray examination of the anhydrous $Na_2SO_4 - Al_2(SO_4)_3$ system. F. A. STEELE, The Pennsylvania State College. (Introduced by Wheeler P. Davey.)—A series of mixtures of Na_2SO and $Al_2(SO)_3$ have been prepared by mixing solutions of the two in known ratios, evaporating to dryness, and heating to 400°C to give anhydrous crystals. X-ray diffraction patterns made by the powder method showed the presence of a definite compound of the composition represented by the formula $NaAl(SO_4)_2$. Specimens containing more $Al_2(SO_4)_3$ than the compound gave the patterns of $Al_2(SO_4)_3$ and $NaAl(SO_4)_2$ superimposed, with no observable change in the parameters of either. Specimens containing an excess of Na_2SO_4 gave the pattern of $NaAl(SO_4)_2$ with additional lines not due to Na_2SO_4, indicating a second compound. The composition of this compound has not yet been determined, but it contains more Na_2SO_4 than represented by the formula $Na_3Al(SO_4)_3$. None of the compounds involved gave patterns similar to soda alum.

34. The crystal structure of strontium-oxide. THOMAS A. WILSON, General Electric Co and Union College.—Powder photographs of samples of SrO were made with Mo K radiation. All the material examined contained $SrCO_3$ as shown by the presence of the spectrogram of the latter. By comparing the spectrograms of $SrCO_3$ and the mixture of SrO and $SrCO_3$ for both position and intensity of the lines, the pattern of SrO was isolated. The lattice is of the NaCl type. The length of the cube edge is $5.073 \pm .01$A, the density is 5.235. Gerlach's values are $5.104 \pm .01$ and 5.143 respectively. (Zeit. f. Phys. **9**, 184 (1922).) All these x-ray values of the density are much higher than those obtained by direct measurement. (Groth gives 4.750.)

35. The oxidation of ferrous sulphate in aqueous solution by x-rays of different wave-lengths.—A determination of the Compton absorption. HUGO FRICKE, Cleveland, Ohio.—The amount of ferrous sulphate oxidized by x-rays to ferric sulphate is determined, the rays being measured in terms of the ionization of 1 cc of air, and is found independent of the concentration of ferrous sulphate (1/100 to 1/25000n). It is concluded that the transformation is due to a primary production of activated water molecules and using Duane and Scheuers determination of the number of water molecules transformed to hydrogen and oxygen by α-rays, it is found that in solutions containing dissolved oxygen, for each such "activated" water molecule $8.2(\pm 2\%)$ ferrous ions are transformed, 2.05 oxygen molecules being simultaneously reduced; in gas free solutions 4.1 ferrous ions are transformed. To ferrous sulphate solutions are added salts of different light elements and for each solution a comparison is made of the amounts of transformation produced by a constant dose of x-rays of different wave-lengths (.20 to .80A). The amount of transformation is independent of the wave-length when the mass coefficient of photo-electric absorption of the solution is equal to that of air, but when larger the effect of the shorter wave-lengths becomes increasingly smaller. This is due to the Compton effect and for $\lambda = .204$ the mass coefficient of absorption due to the production of Compton electrons is for light elements found equal to .0158; the value derived theoretically by Compton is .0156.

36. Reflection of soft x-rays from aluminum. S. D. GEHMAN AND C. B. BAZZONI, University of Pennsylvania.—Non-characteristic soft x-rays, of voltage range 40 to 300, were passed through a slit system and then reflected from a polished aluminum mirror in a high vacuum. The reflecting power of the mirror was measured by a photo-electric method as a function of the voltage for a given grazing angle and as a function of the angle for a given voltage. The reflecting power-voltage curve shows a broad maximum between 68 and 140 volts accelerating potential and falls off rapidly as the voltage increases. It is hoped to resolve this maximum to give critical potentials of aluminum by filtering or otherwise. For a fixed voltage the reflecting power falls off rapidly as the grazing angle increases. With a plate voltage 102, for example, the reflecting power for a grazing angle 9 degrees 30 minutes was 0.460, while for an angle of 12 degrees 30 minutes it was 0.140. The form of the reflecting power-grazing angle curve is practically independent of the voltage.

37. Refractive indices of silver in the wave-length range of two to seven Angstrom units. ELMER DERSHEM, University of California.—The indices of refraction of silver have been measured at short wave-length intervals in this region, using the same methods previously reported (Phys. Rev. **31**, 305 (1928) and Bull. Am. Phys. Soc. Vol. **3**, No. 2, Feb. 18, (1928)). The dispersion curve thus obtained shows a marked depression in the values of δ on both sides of the L_I absorption limit wave-length. A much greater depression is noted mid-way between the L_{II} and L_{III} absorption limit wave-lengths. Further work is being done to definitely determine whether this effect is caused by the depressions due to latter levels not being resolved or is due to these two levels functioning as one in dispersion phenomena as might easily be expected. While the shorter wave-lengths give values of δ which are in agreement with classical theory if not too near an absorption limit it may be noted that in all substances thus far examined that δ rises rapidly with increasing wave-length between 6 and 7 Angstrom units. δ for platinum increases 51% in this range while δ for silver increases 54%, δ for silver having a value of 666×10^{-6} at 7 Angstrom units.

38. X-ray diffraction in liquids—isomers of normal heptane. G. W. STEWART, University of Iowa.—An examination was made of the diffraction of monochromatic .712A radiation with the following liquids: 2-3, 2-4, 2-3 and 3-3 dimethyl pentane, 2 and 3 methyl hexane, 2-2-4 trimethyl pentane, 2-2-3 trimethyl butane, and 3 ethyl pentane. The general conclusion is that the isomers differ from the normal compounds in a manner similar to that occurring in the alcohol chains. The effect upon the "diameter" of the molecule of the group CH_3 in a branch depends upon the number of groups and the points of attachment. The "straightness" of the chain itself is modified by the attachment of branches. With 3 ethyl pentane where the molecule is a union of three like branches, a symmetrical form is indicated. The length of the normal paraffin chains is expressed with less than one percent accuracy by $1.24n+2.70$ Angstroms wherein n is the number of carbon atoms. The comparison of all data from this laboratory on the x-ray diffraction in liquids indicates that the use of Bragg's law and the interpretation of the liquid condition as the cybotactic state is justified.

39. K-electron ionization by direct impact of cathode rays. DAVID L. WEBSTER, Stanford University.—Investigations reported at the Reno meeting (Proc. Nat. Acad. Sci., **13**, 445 (1927)) on the ratio of direct and indirect characteristic rays of silver, have been improved and extended. Between 35 kv and 80, although the rays increase in intensity by factors of 18 or 19, this ratio changes very little, the data giving 1.83 to 1.96, each $\pm 10\%$. The probability that a cathode ray will ionize a K electron by direct action, i.e., action all within one atom, bears a ratio of 0.90 to the probability that it will emit a corresponding quantum of continuous spectrum radiation; this ratio is constant with change of voltage, and therefore applies to thin targets also. The absolute probability of direct K ionization can be calculated by combining present data with total x-ray efficiency data, with results confirming Thomas' theory. This and other evidence indicates that the direct process of K-electron ionization is not an internal photo-electric effect so often as it is a repulsion, much like ordinary electrostatic force.

40. Atomic structure factor and Fourier analysis. G. E. M. JAUNCEY AND W. D. CLAUS, Washington University, St. Louis.—Compton (X-Rays and Electrons, p. 164) gives a formula for the radial distribution (U) of electrons in an atom. When $D\rightarrow\infty$, U takes the form of the Fourier integral

$$U(r)=8\pi r\int_0^\infty xF(\lambda x/2)\sin 2\pi rx\,dx \qquad (1)$$

where F is the atomic structure factor expressed as a function of $\sin\theta$. For the case of Z electrons moving in a circular orbit of radius c in an atom and the atom vibrating thermally so as to give a Debye temperature factor of $\exp(-b\sin^2\theta)$ we obtain

$$U(r)=(Z/ac\sqrt{\pi})r\{\exp[-(r-c)^2/a^2]-\exp[-(r+c)^2/a^2]\} \qquad (2)$$

where $a=(\lambda\sqrt{b})/2\pi$ = the most probable displacement. Using the experimental value of b at room temperature for rocksalt, $a=0.175$A in good agreement with James and Firth's value of 0.20A (Proc. Roy. Soc. A, 117, 62). We have compared a U curve obtained from (1) with a U curve obtained from Compton's formula for a model Cl^- atom and we find that the positions of the maxima agree. A U curve gives the electron distribution relative to a lattice point of the crystal and not relative to the center of the atom.

41. Fine structure in the K-series of copper and nickel. HARRIS PURKS, Columbia University.—High resolving power was obtained by means of the double x-ray spectrometer with crystals set so as to increase the angular displacements. The method was the same as that previously described by Davis and Purks (Proc. Nat. Acad. Sci. June, 1927, and Feb., 1928). With both crystals set for first order reflection there appeared bulges on the long wave-length sides of the Kα lines of copper and nickel. It was found that these bulges could be explained as weak lines at displacements of .42 X.U. and .35 X.U. to the long wave-length sides of Cu Kα_1 and Cu Kα_2, respectively, and .45 X.U. and .38 X.U. to the long wave-length sides of NiKα_1 and NiKα_2 respectively. These results were checked by placing both crystals at second order. At second order there appeared evidence of other structure nearer the center of the principal lines. The Kβ doublets of these elements were investigated. They were not

resolved but the rocking curves by their shape permitted solutions of the problem of displacements and intensities of components. The separations graphically determined from the curves were CuKβ .32 X.U., Ni Kβ .29 X.U. It was found that the widths of the lines were dependent upon the voltage across the tube. Near the excitation voltage the widths were about two-thirds that at 40 kv.

42. Effect of chemical combination on the structure of the K absorption limit of silver and molybdenum. BERGEN DAVIS AND HARRIS PURKS, Columbia University.—The proper arrangement of crystals in the double x-ray spectrometer has multiplied the resolving power of ionization spectrometer many times. By its use fine structure in the K series of Mo, Cu and Ni have been discovered. The structure of the absorption limit was investigated by the same method. The limit of the pure metal is quite sharp. Its total spread (Ag and Mo) is less than .5 X-units. The limit for Ag_2S and Ag_2O was broader than for the pure metal. Also Ag_2S showed traces of structure and Ag_2O showed marked evidence of structure. The Ag_2S turned black indicating dissociation by the x-rays. The limit for MoO_3, MoS_2 and Mo_2O_3 was investigated. All of these compounds showed marked broadening at the limit. Marked evidence of structure was observed in Mo_2O_3. The center of gravity of the limit is not much shifted. The K limit of copper was also taken. It was much wider than in the case of Ag and Mo. In general the absorption limit broadens toward lower atomic numbers. The copper compounds were not investigated as energy available was too small. The measurements were all made with both crystals at first order.

43. Fine structure of scattered x-rays. DANA MITCHELL AND BERGEN DAVIS, Columbia University.—By means of a double x-ray spectrometer with calcite crystals the fluorescent radiation from a sheet of molybdenum was observed. The Kα doublet was resolved into two lines less than .5 X.U. wide at their half maximum. The Mo Kα_1 scattered at approximately 90 degrees by a piece of carbon was then investigated. Five lines attributable to Mo Kα_1 were found. One is in the position of the fluorescent Mo Kα_1, and three are displaced by 1, 2, and 10 X.U. from the unmodified in the long wave-length direction. The width at half maximum of each of these is .6 X.U. or less. The fifth line about 4 X.U. wide at half maximum and displaced about 22 X.U. seems to be the modified line in the Compton effect. Assuming the impulse of the deflected quantum to be absorbed by the atom and the scattering electron to be removed from one of the L positions of carbon the displacements of 1 and 2 X.U. are each about twice that predicted by the expression $\Delta\lambda=\lambda^2/(\lambda s-\lambda)$. The displacement of 10 X.U. is a little less than similar assumptions predict for the case of a K electron in carbon.

44. X-rays from thin targets. WARREN W. NICHOLAS, National Research Fellow, Cornell University.—Very thin metal foils are mounted as anticathodes in x-ray tubes. The thickness of the foils is such as neither to slow up nor to deflect the cathode rays appreciably at the voltages used. Thus the x-rays produced in the foil result from the bombardment of atoms by cathode rays of uniform speed and direction. The spectra of these x-rays are examined photographically by means of small Seeman spectrographs placed inside the x-ray tube. The continuous spectra in different directions relative to the cathode stream differ markedly as to spectrum energy distribution. Due to the simplicity of the photographic blackening laws for the x-ray region, quantitative results are obtainable by the method, and on account of the simplicity of the present conditions as compared with the conditions in the ordinary thick target x-ray tube, it is expected that these results will yield to a more direct theoretical interpretation. Spectrographs and densitometer curves are reproduced for a comparison of thick and thin target spectra, as well as for comparison of thin target spectra in different directions, and these are discussed in the light of present theories.

45. The scattering of x-rays from gases. CHARLES S. BARRETT, University of Chicago.—Using apparatus previously described (Proc. Nat. Acad. Sci., **14,** 20 (1928)) with unfiltered Mo rays from a Coolidge tube at 62000 volts, the azimuthal distribution of intensity of scattering from gases was measured. The scattering from helium coincides with that from hydrogen (proportional to $1+\cos^2\theta$) from 60° to 100° but is slightly greater from 20° to 60°. The deviation at the small angles is of the type that could be explained as due to a small amount of nitrogen

as an impurity. Nitrogen shows excess scattering, though at somewhat smaller angles than oxygen. Argon exhibits excess scattering over the whole range investigated, 20° to 100°. Reduced to equality with hydrogen at 100°, its intensity at 40° is over twice that of hydrogen. This does not confirm Mark and Schocken's finding of $(1+\cos^2\theta)$ for argon. The scattering from argon at angles less than 100° increases with increasing wave-length giving further evidence of coherent scattering. These experiments with argon show the existence of excess scattering from atoms spaced at random. Scattering which follows the $(1+\cos^2\theta)$ formula may be considered as modified, as this formula expresses the predictions of the quantum theories within experimental error.

46. The polarizing angle for x-rays. G. E. M. JAUNCEY AND GERALD HASSLER, Washington University, St. Louis.—The classical theory of x-ray scattering and the theory based on the new quantum mechanics predict 90° for the polarizing angle, while the quantum theories of Jauncey and Compton give a polarizing angle of less than 90° and dependent upon wave-length. Jauncey and Stauss found a polarizing angle of less than 90° for an effective wave-length of 0.25A scattered by paraffin (Phys. Rev., **23,** 762 (1924)) while later Bearden and Barrett (Phys. Rev., **29,** 352 (1927)) find a polarizing angle of 90° or slightly greater than 90° for a wave-length of 0.215A. We have repeated the experiments of Jauncey and Stauss with a wave-length of 0.27A and we find a polarizing angle of 90°20′ thus supporting the findings of Bearden and Barrett.

47. The diamagnetic layer of the earth's atmosphere and its relation to the diurnal variation of terrestrial magnetism. ROSS GUNN, Naval Research Laboratory, Washington, D. C. (Introduced by Lynde P. Wheeler.)—An examination of the phenomena existing in the upper layers of the earth's atmosphere shows that ions or electrons in motion spiral about the earth's magnetic field producing certain electrical and magnetic effects which modify greatly present ideas regarding this layer. Maintained ionization of the layer is great only in the regions where the free paths of the ions or electrons are long. Under the condition of long free paths the electrical conductivity is anisotropic. Large circulating currents in the upper atmosphere of the type assumed in present theories of the diurnal variation are shown to be highly improbable. A new theory of the diurnal variation of the earth's magnetic field is proposed which appears to be free of objectionable assumptions and explains quantitatively the major features of the observed facts. As a consequence of the theory and experimental data it appears that an appreciable fraction of all molecules in the upper atmosphere having long free paths are ionized.

48. Capacity of aluminum anodes. J. E. LILIENFELD, Washington Square College, New York University.—Two different theories have been advanced in order to explain the action of the aluminum cell. Both agree that aside from the oxide layer formed on the aluminum anode there is also a gas layer (or some other invisible layer, Slepian) present. They differ with respect to the question whether exclusively the gas layer is responsible for the observed phenomena (Gunther-Schulze); or whether the influence of the oxide layer upon the electrical characteristic is to be considered alongside with that of the gas layer. (Guthe; Fitch; Meserve.) The idea of a gas layer has been introduced—among other reasons—because it is being assumed that the visible oxide layer by itself may not account for the capacity of the cell. However, it has to be mentioned that with respect to the resistance of the cell there is on the part of Fitch and Meserve a tendency to consider the oxide layer as the determining factor. The present investigation adds to the knowledge of this class of phenomena by showing that the dielectric dry oxide layer as formed in the electrolytic cell upon application of a definite maximum voltage will, if properly brought into contact with a metal, form a specific capacity controlled to a large extent by that voltage and checking within close limits some of the figures of Gunther-Schulze. For instance: for a 325V layer Gunther-Schulze quotes 0.018μF while 0.017μF have been measured in the present case.

49. Measurement of the charge of positive ions by the shot effect. N. H. WILLIAMS AND W. S. HUXFORD, University of Michigan.—Following somewhat similar methods to those used by Hull and Williams in measuring the electronic charge in thermionic and photo-electric

emissions, the charge of the positive ion in high vacuum has been measured. The amplifier consists of five stages in which shielded grid tubes are used with tuned plate circuits. The source of positive ions was a fused mixture of potassium and iron oxides. A formula developed in a paper by Williams and Vincent expresses the electronic charge in terms of the impedance, Z, of the circuit and the area, A, under the resonance curve of the amplifier. This equation is $e=v^2/2Z^2i_0A$, where v is the high frequency voltage which produces the same effect upon the amplifier as the shot voltage and i_0 is the space current through the tube as read from a microammeter. This equation was used in computing the positive ionic charge. The measurement of Z is accomplished by an improved method of considerable precision. The result is a numerical value equal in magnitude to the charge of the electron within the limit of error of the frequency standard used.

50. The refraction of electrons by a crystal of nickel. C. J. DAVISSON AND L. H. GERMER, Bell Telephone Laboratories, Inc.—New electron diffraction measurements, made by a method entirely analogous to the Bragg method of x-ray spectroscopy, have shown a selective regular reflection of electrons from a $\{111\}$ face of a nickel crystal for a series of different critical electron speeds. These selective reflections correspond to various orders of the Bragg reflection of x-rays. The electron wave-lengths do not, however, coincide with the critical wave-lengths for the corresponding x-ray reflections, but at high voltages they approach these wave-lengths. We have found two angles of incidence (10° and 46°) for which adjacent orders occur at the same electron wave-length (1.07A). These observations allow us to determine the orders of the electron reflections, and to show that the differences between critical electron and x-ray wave-lengths can be accounted for by attributing to the crystal a refractive index varying regularly from 1.13 at 1.6A to 1.01 at 0.5A. The differences cannot be accounted for by assuming a superficial spacing factor or a refractive index less than unity. This assignment of orders corresponds to the second of the two possible associations of electron beams with x-ray beams considered heretofore (Phys. Rev., **30,** 705 (1927)). This seems now to be established as the correct association.

51. Interaction of electron and ion space charges in cathode sheaths. IRVING LANGMUIR, General Electric Co.—The usual space charge problem for electrons from a plane hot cathode to a parallel plane anode is modified by assuming positive ions emitted from the anode. Single ions emitted with negligible velocity permit $0.378(m_p/m)^{1/2}$ additional electrons to pass. An unlimited supply of ions gives an electron current 86.05 percent greater than with no ions, the field is symmetrically distributed between cathode and anode, and the electron current is $(m_p/m)^{1/2}$ times the ion current. These conditions apply to a cathode emitting a surplus of electrons surrounded by uniformly ionized gas. The cathode sheath is a double-layer with an inner negative space charge and an equal outer positive charge, the field being zero at the cathode and at the sheath edge. The electron current is limited to $(m_p/m)^{1/2}$ times the rate at which ions diffuse to the sheath edge and is independent of voltage if the source of ions is constant. Experiments with oxide cathodes in mercury vapor agree with this theory. The theory has been extended to take into account initial velocities of ions and ultimate electrons and also to deal with cylindrical sheaths.

52. Some characteristics of the discharge between cold electrodes in vacuum. ALBERT W. HULL AND E. E. BURGER, General Electric Co.—*Heavy discharges* from a transformer or charged condenser were passed between well-exhausted solid tungsten electrodes 2 mm apart in a good vacuum. *Current-time* and *voltage-time characteristics*, taken with a cathode ray oscillograph, show that the current starts as a pure electron discharge, but soon changes to a tungsten vapor arc. The arc voltage is less than 1000 with discharge currents as high as 20,000 amperes. Condenser charges of 5000 joules energy (1 microfarad at 100,000 volts) can thus be discharged through the tube repeatedly, with no appreciable heating of the electrodes. As soon as the discharge ceases the tungsten vapor condenses, and the breakdown voltage returns to its original value. The *time-lag* in passing from pure electron discharge to arc is less than 10^{-7} sec. The time lag in passing back again from arc to pure electron discharge depends on the depth of penetration of the heat. With heavy discharges it is between 1 and 10 microseconds. The *voltage gradient* necessary for breakdown is about 500,000 volts per cm for tungsten, and 100,000 for carbon.

53. Heats of condensation of electrons on platinum in ionized He, Ne and A. C. C. VAN VOORHIS AND K. T. COMPTON, Princeton University.—The heat liberated by the absorption of electrons at the surface of a Pt electrode was measured by the method previously described (C.C.V.V., Phys. Rev., **30,** 318 (1927)). Platinum is notoriously difficult to obtain with a clean surface, hence extreme measures for purifying the metal and gases were employed. The results obtained are: ϕ (Pt in A), 5.20 volts; ϕ (Pt in Ne), 5.00 volts; ϕ (Pt in He), 4.77 volts. These are relatively accurate to within a small fraction of a percent, but the absolute values may be high by not more than five percent owing to possible loss of weight of the electrode during an over-strenuous positive ion bombardment for cleansing purposes preceding the series of measurements. Correction for this error will be made later. Contrary to general belief, the work function of the metal in these inert gases varies with the gas used. This had been suspected in the earlier work with molybdenum but was not then thoroughly investigated. Experiments in mixtures of these gases at different voltages prove that it is the *ions* rather than the neutral atoms which influence the work function—a result suggestive of the halogen-like character of the rare gas ions.

54. The reflection of hydrogen atoms from crystals. THOMAS H. JOHNSON, Bartol Research Foundation of Franklin Institute.—Recent theories, as well as the experiments of Davisson and Germer suggest a wave of length $\lambda = h/mv$ associated with a freely moving particle. Evidence for the existence of such waves associated with the hydrogen atom has been sought by reflecting atomic hydrogen from a Wood tube from various crystal surfaces. Diffraction lines from a powdered crystal surface of ice, if present, were masked by scattered atoms although these were less than 1/300 as intense as the incident beam. Freshly cleaved rock salt, heated to degasify, reflects intensely with angle of reflection equal to the angle of incidence. Prismatic and hexahedral faces of crystal quartz, and freshly cleaved calcite reflect in no preferred direction. First order surface grating beams from rock salt were looked for but if they existed they were masked by the general reflection.

55. Phenomena at the cathode of a mercury arc. THOMAS J. KILLIAN, Princeton University. —The region close to the cathode in a mercury arc was investigated by the use of small cylindrical collectors after the method of Langmuir (G. E. Rev. (1924)). The space potential at distances of from 0.2 cm to 3 cm from the cathode spot was found to vary from 10.1 volts to 11.6 volts above that of the cathode. The cathode drop is therefore probably very close to 10 volts. The only previous determination of the cathode drop made by Stark (Ann. d. Phys. (1905)) was 5.27 volts. However, this is not the space potential but that at which equal numbers of electrons and positive ions are collected. The random positive ion currents were between 1.5 and 40 milliamps cm^{-2}. Random electron currents of from 1.3 to 18 amperes cm^{-2} and temperatures of from 5000°K to 16,500°K were also measured. The cathode is covered by a thin positive space charge sheath which seems to be punctured at the cathode spot due to the large electron emission at this point. Evidence is presented that these electrons are not of thermionic origin. An attempt is being made to conduct the investigation even closer to the cathode spot.

56. Ionic oscillations in the glow discharge. J. S. WEBB AND L. A. PARDUE, Lehigh University. (Introduced by C. C. Bidwell.)—In an effort to correlate Whiddington's work on moving striae and Appleton's work on ionic oscillations from a striated discharge, it was found that the ionic oscillation phenomenon was sufficiently involved to warrant a detailed study. The discharge tube was of the hot cathode type, 3 centimeters in diameter and 26 centimeters long. The oscillations were detected in three ways; first, by means of curved plates on the tube which were connected in parallel with the tuning condenser of the receiver; second, by direct inductive "pick-up" from the tube itself; third, by inductive "pick-up" from a coil in series with the tube. By these methods frequencies from 240000 to a few hundred cycles were obtained, the higher frequencies being detected on an auto-dyne receiver, the lower frequencies, on a straight low frequency amplifier. Characteristic curves obtained show an increase of frequency with filament current, an increase of frequency with anode potential, and a decrease

with pressure except at the highest and lowest pressures where decided minima and maxima respectively occur. Without plates on the tube oscillations do not occur in sharply defined striae but begin just as striae commence diffusing, decreasing in frequency and become audible when a uniform glow fills tube.

57. Electrical breakdown of spark gaps at atmospheric pressures. J. SLEPIAN, West. Elec. and Mfg. Co., East Pittsburgh.—As shown by Rogowski, the classical Townsend theory applied to breakdown of spark gaps at atmospheric pressures leads to time of breakdown greater than 10^{-5} sec. for gaps 1 cm or more in length, whereas experiments show times of the order of 10^{-7} sec. It may be shown by calculation, using values of ionizing constants derived from low pressure experiments, that the initiating electron, in its motion towards the anode accompanied by the electrons generated by collisions will so raise the temperature of the gas that the path left behind will be thermally ionized. In this way the need for the repeated traversal of the path by positive ions is obviated, and the short time for breakdown accounted for. Taking the effect of space change into account, and assuming that the critical gradient for sparkover is that at which thermal ionization first appears, a satisfactory agreement is found with the observed critical gradient as a function of gap length at atmospheric pressure. The formation of streamers during breakdown as disclosed by Torok is also explained.

58. The formation of atomic negative ions in mercury vapor. WALTER M. NIELSEN, Duke University.—A beam of electrons was projected along the axis of a discharge tube, coaxially placed inside a solenoid which produced a magnetic field of 250 gauss. Negative and positive ion currents produced in a definite length of the beam were measured for different driving potentials by applying suitable potentials to electrodes on opposite sides of the electron beam. The total current was absorbed by an end plate, placed perpendicularly to the magnetic field. Secondary electron effects were eliminated by a 115 volt accelerating potential on the end plate. The curves giving the relationship between the ratio of negative ion to total current as a function of the driving potential show that: At a vapor pressure corresponding to saturation at 14°C, the probability of the capture of a slowly moving electron by a normal atom is small compared with the probability of the attachment of an electron to an excited mercury atom. The following critical potentials for negative ion formation were observed: 4.7, 5.3, 6.0, 7.3, 8.8, 9.3, and 11.4 volts. Under the above conditions, a relatively small number of negative ions was observed at 2.3 and 2.7 volts. They are believed to be due to the mercury molecule and will be discussed in another paper.

59. Platinum term values and classification. PAUL J. OVREBO, University of Chicago. (Introduced by H. G. Gale.)—Forty new intermediate and upper levels together with three new low levels have been found for platinum. Combinations of these and of levels previously known give 142 lines. A. C. Hausmann's classification of the old low levels from the Zeeman effect is taken as the basis for prediction of classification of some of the new levels and of the unclassified old intermediate and upper levels. These assignments agree with Hausmann's assignment of j values for the old levels. The number of platinum lines classified now total 500. This leaves about 200 lines to be classified, excepting the lines of very low intensity. The work on these lines is in progress. This work assumes that Kayser's wave-lengths are accurate to .05A.

60. The spectra of cadmium II, arsenic IV, arsenic V, and selenium V. R. A. SAWYER AND C. J. HUMPHREYS, University of Michigan.—Extrapolation of the screening constant data for the $^2D(d^9s^2)$ term in 47 electron spectra, and the $^3D(d^9s)$ term in 46 electron spectra has permitted the prediction and location of the analogous ^2D term in the spark spectrum of cadmium. New vacuum-spark data in the extreme ultra-violet has been obtained for arsenic and selenium. By aid of previous classifications in 29 and 30 electron spectra of copper, zinc, gallium, and germanium, it has been possible, by aid of extrapolation of the Moseley diagram the irregular doublet law, screening constant data, and the triplet interval ratios, to predict the location of and to identify the multiplets arising from the lowest levels in the spectra of arsenic IV, arsenic V, and selenium V. The power of these methods is again demonstrated by the accuracy of the predictions. The 4^2S term of arsenic V is determined as about 505100 corresponding to an ionization potential of 62.4 volts.

61. The spectrum of quadruply ionized tin, Sn V. R. C. GIBBS AND H. E. WHITE, Cornell University.—It has been shown in passing from element to element in certain sequences of iso-electronic systems that when an electronic transition takes place between two levels having the same total quantum number, the resulting lines are displaced to higher and higher frequencies by very nearly a constant value. Applying this general rule to the spectra of Pd I, Ag II, Cd III, and In IV, and guided by the Moseley type of diagram for the values of $(\nu/R)^{1/2}$ of the terms, by term separations, and by relative intensities, we have been able to identify most of the strong lines in the spectrum of Sn V. The lines arising from the transitions $^3PD'F$ and $^1PD'F(4d^95p)$ into ^3D and $^1D(4d^95s)$ are found in the region 1000 to 1500A. The lowest energy level of the spectrum $^1S_0(4d^{10})$ has been identified by transitions from $^1P_1$, $^3P_1$, and $^3D_1'(4d^95p)$. These three lines were found in the region of 360A, each within one Angstrom of the wave-length predicted from an extrapolation of the $^1S_0$ and $^1P_1$ lines on a Moseley diagram for the Pd I-like sequence.

62. An analysis of the arc and spark spectra of yttrium. WILLIAM F. MEGGERS, Bureau of Standards, and HENRY NORRIS RUSSELL, Princeton University.—An analysis of the arc and spark spectra of scandium was reported by the authors last year (Phys. Rev., **29**, 606 (1927)); a similar analysis of the analogous spectra of yttrium has now been completed. Both spectra of yttrium were entirely remeasured, a satisfactory separation of the Yt I and Yt II lines was obtained, and many new lines were recorded. Practically all of the lines in both spectra have been classified and series forming terms have been identified in each. The spectral series give an ionization potential of 6.6 volts for the neutral Yt atom, and 12.3 volts for the Yt^+ atom. Although a striking similarity exists between the yttrium spectra and the corresponding spectra of scandium, there are some important differences. For example in the Yt II spectrum, a singlet-S term $(5s)^2$, not observed in Sc II, is slightly lower in energy than $^3D(5s\cdot 4d)$. The analysis is supported by measurements of Zeeman effects photographed for this purpose by the late B. E. Moore. All details of the Yt I and Yt II spectra are in accord with Landé's theory of Zeeman effects and with Hund's theory of spectral terms.

63. The application of the x-ray laws to optical spectra of higher rank, and the classification of Ga IV and Ge V. J. E. MACK AND OTTO LAPORTE, University of Michigan, and R. J. LANG, University of Alberta.—X-ray energy levels are ionization energies of neutral atoms, whereas in isoelectronic sequences the net charge increases with the atomic number Z. The first order screening number σ_1, for a given electron, increases with Z in x-ray spectra but decreases to an asymptote in isoelectronic spectra; the difference is probably due to outer screening. Exact representation of isoelectronic optical spectra on a Moseley diagram, generally, requires knowledge of series limit correlation of individual levels. If σ_1 for a certain electron is plotted as a function of Z in several isoelectronic sequences, the initial slopes of the resulting curves depend only slowly upon the total number of electrons, and for a given total number of electrons the slope is substantially independent of the configuration; this implies that the lines on a Moseley diagram representing the addition of a given n_l electron to different isoelectronic sequences containing nearly the same number of electrons, are parallel, to a second approximation. The irregular doublet law applied to isoelectronic sequences in the neighborhood of a closed d-shell (d^{10}) is valid for $\sqrt{p}-\sqrt{s}$ but not for $\sqrt{d}-\sqrt{p}$ or for $\sqrt{f}-\sqrt{d}$. By application of the x-ray laws the $(3d^94s)$ and $(3d^94p)$ levels of Ga IV and Ge V have been found. From a comparison of the spectra Ni I to Ge V, it appears that $^3D_2(3d^94s)$ should be correlated with the series limit $^2D_3(3d^9)$, contrary to the theory of Hund.

64. Disagreements with the predictions of the Hund theory of series limits. A. G. SHENSTONE, Princeton University.—The Hund theory includes a prediction of the individual levels of an ion to which component sequences will converge. The theory is reasonably confirmed in the case of spectra determined by less than half-filled electron groups. For spectra determined by almost complete groups, there are, in addition to a large amount of adverse though inconclusive evidence, two definite cases of disagreement. The first case is the ^3P, $^1P(p^5s)$ sequences of NeI. The four component series actually converge to the ^2P limit in pairs $^3P_2$, $^3P_1$; $^3P_0$, $^1P_1$: theoretically $^3P_2$, $^1P_1$; $^3P_1$, $^3P_0$. The second case is the ^3D, $^1D(d^9s)$ sequence in

PdI where the convergence is actually in pairs $^3D_3$, $^3D_2$; $^3D_1$, $^1D_2$: theoretically $^3D_3$, $^1D_2$; $^3D_1$, $^1D_2$. The nature of these terms was fixed by intensities from McLennan and Smith's analysis, and the terms agree only partially with their identifications. The disagreements between the Hund theory and the experimental results are a real difficulty since the predictions of the theory are definite and there seems no part of the argument where ambiguity may enter.

65. Zeeman effect of hyperfine structure and magnetic moment of the bismuth nucleus. E. BACK, University of Tuebingen, Germany, and S. GOUDSMIT, University of Michigan.—The analysis of the hyperfine structure of the bismuth lines and energy levels has shown that the bismuth nucleus very probably possesses a mechanical moment of momentum and a magnetic moment. The Zeeman effect in strong fields (43000 gauss) gave for the *mechanical* moment of the nucleus the value $9/2 \cdot h/2\pi$ (Zeit. f. Phys., **43,** 321 (1927) and **47,** 174 (1928)). The *magnetic* moment can, however, not be derived from those Zeeman effects, as its value just cancels out in the results. Preliminary observations of the Zeeman effect of λ4121 in weak fields (8000 gauss) were made by E. Back. The magnetic moment could not be detected, meaning that the ratio between magnetic moment and mechanical moment (Landé g factor) must be smaller than 1/10 in quantum units. Thus the nuclear moment is very probably not produced by moving or spinning electrons in the nucleus (expected $g \sim 1$), but by positive particles ($g \sim 1/10000$). This result is in agreement with the order of magnitude of the natural hyperfine structures in bismuth without magnetic field.

66. Multiplet separations. S. GOUDSMIT AND C. J. HUMPHREYS, University of Michigan.—Formulas for the separations of normal multiplets, arising from general configurations, are derived by reasoning from the fundamental assumption that they are due to the interaction energy between spin and orbital magnetism of the electrons. The separations are known for multiplets arising from groups of equivalent electrons, from considerations given in another abstract. It can be shown by a simple treatment of the vector model that the interaction energy for other configurations may be found in terms of that of the equivalent group and the interaction energy of the electron or group of electrons added, provided the quantum vectors of the original configuration remain unchanged. Our treatment applies only to multiplets showing reasonably close agreement with the interval rule, and which are therefore accounted for by the Russell-Saunders coupling. Applications to known spectra indicate the validity of our formulas to the extent permitted by agreement of data with the interval rule. The formulas also can be used to determine the electron configuration from the observed multiplet separations.

67. The comparison of the long and short arcs as an aid in the analysis of spectra. KEIVIN BURNS, Allegheny Observatory, and F. M. WALTERS, JR., Carnegie Institute of Technology.—Any data which aids in sorting the lines into different groups is of assistance in finding regularities in a spectrum. In iron a comparison of the long and short arcs enables one to pick out spark lines, lines which are broadened in the short arc, groups of lines shifted to the red and lines shifted to the violet. Self-reversal is far more pronounced in the short arc than in the long arc. The advantages of this method are that it may be used for the study of weaker lines than are usually observed and that it does not require the use of special equipment other than a large grating in a stigmatic mounting.

68. A type of variation from Beer's law and some of its implications. C. V. SHAPIRO AND R. C. GIBBS, Cornell University.—Deviations from Beer's Law ordinarily occur if chemical reactions take place in a solution upon changing the concentration. Hydrolysis is a typical equilibrium reaction dependent on concentration and occurs in the case of solutions of the salts of weak acids and bases. Data is presented to show the effect on absorption spectra of diluting alkaline solutions of weak acids of the phthalein and fluorescein series while maintaining the ratio of alkali to acid constant. In the light of this data, the interpretation of absorption spectra and their bearing on chemical constitution are discussed. Fluorescence is also affected under these circumstances, since the phenomenon of luminescence is dependent both on the nature of the active ions in solution under the particular conditions of concentration of alkali and active substance employed and on their absorption under these conditions.

69. Active nitrogen. JOSEPH KAPLAN, National Research Fellow in Physics, Princeton University.—It was observed in the present experiments that the fourth positive group of nitrogen was excited in a weak discharge through active nitrogen. The passage of a weak discharge through active nitrogen, as Strutt has found, results in the partial destruction of the afterglow. The above bands were observed whether the active nitrogen was made from air or from commercial nitrogen. Strutt observed that the main difference between a condensed and an uncondensed discharge in nitrogen was the presence of the fourth positive group in the former. The same observation has been made by the author for discharges through air. It is suggested that the fourth positive bands in the condensed discharge and in the weak discharge through active nitrogen are excited in the same manner. The fourth positive group corresponds to the transition D–B in the nitrogen molecule, where the D level is the highest electronic level of the molecule. The excitation of these bands under the present conditions may indicate the presence of metastable molecules in the afterglow.

70. The excitation of oxygen by active nitrogen. JOSEPH KAPLAN, National Research Fellow in Physics, Princeton University.—A green line of oxygen of wave-length 5578A, which is now thought to be the Aurora green line, and a red line of oxygen at wave-length 6655A have been observed in the afterglow of active nitrogen. Preliminary experiments on the excitation of the green line show that an N_2 mixture containing about 4% oxygen is best for the excitation of the line. Active nitrogen produced in this manner shows an unusual development of the α bands of N_2. In addition to the prominent after-glow bands many of the remaining α bands are strongly emitted under these conditions. The appearance of these two oxygen lines alone, without the presence of the strong arc lines, suggests that they are excited in a simple process. Further experiments are necessary, however, before a definite process of excitation can be proposed.

71. The rotational structure of the blue-green bands of Na_2. R. W. WOOD AND F. W. LOOMIS, the Alfred Loomis Laboratory, Tuxedo Park, N. Y.—Owing to the theoretically impossible structures of these bands as reported by previous observers the writers have measured them, in absorption, in the third order of a seven inch plane grating mounted in the forty foot spectrograph. Each band is found, quite definitely, to consist of only one P, one Q and one R branch. This accords with Mulliken's theory that the electronic transition is $^1P-{}^1S$, and with the evidence of the fluorescent series. The combination relations have been applied to all measured bands and found to hold, rigorously, within the experimental error, except for the expected P,Q,R defect. This can be represented by values of B' which differ slightly in the P and R branches from those in the Q branches. The more important constants of this band system are: $B_0''=0.15431$ cm, $r_0''=3.08\times10^{-8}$ cm, $\alpha''=0.00082$, $B_0'=0.12541$ cm, $r_0'=3.41\times10^{-8}$ cm, $\alpha'=0.00094$, $B_{PR}'-B_q'=0.000013$. These extremely large internuclear distances correspond to very weak molecular binding, which is in accord with the low heat of dissociation previously reported.

72. Thermoelectric power of selenium crystals. R. M. HOLMES AND A. B. ROONEY, University of Vermont.—Crystals were formed by slow condensation of the vapor in a tube evacuated to .008 mm, one end of the tube being in an oven with automatic temperature control while the other end was in open air. The best crystals grew on a fine thread of pyrex glass situated in the center of the tube. Thermal e.m.f. measured against copper follows the equation: $E=1.10t+.00017t^2$ in millivolts and between 0°C and 180°C. This is the largest thermal e.m.f. so far reported for any substance and since it is about 800 times the value for a copper-lead couple, the above equation holds equally well for selenium against lead. Thermal e.m.f. is nearly a linear function of t, one junction being at zero, showing that the Peltier effect is responsible for nearly all of the thermal e.m.f. An e.m.f. is developed in some crystals by the absorption of light when the circuit is at a uniform temperature. This actino-electric effect, which is new for single crystals of selenium, amounts to as much as 10 millivolts for a 100 watt lamp at 50 cm and is not due to heating.

73. The thermal e.m.f. and resistance of single crystals of non-cubic metals. P. W. BRIDGMAN, Harvard University.—An improved method of casting single crystals has permitted

the production of crystals with a wider and more uniform distribution of orientations than hitherto, and a reexamination, with greater accuracy, of the way in which thermal e.m.f. and resistance varies with direction. The metals studied were zinc, cadmium, tin, bismuth, and antimony. Except for small, but distinct effects in tin and bismuth, the thermal e.m.f. is a linear function of $\cos^2\theta$, where θ is the angle between the axis of the crystal and the length of the rod. This is the relation of Kelvin and Voigt, about which I have previously expressed doubt. I still can see no theoretical method of deriving the relation. The new results on resistance verify the discrepancy between my former results and those of other observers, in that I find a smaller difference between the resistance parallel and perpendicular to the axis. This can be explained by the difficulty of avoiding slight flaws or slip on the cleavage or slip planes.

74. Thermionic activity, evaporation, and diffusion of barium on tungsten. J. M. EGLIN, Bell Telephone Laboratories, Inc.—When a tungsten filament is being coated with barium in a vacuum, the thermionic electron emission increases at first, reaches a maximum with a definite amount of coating, and then decreases again. The Richardson line for the maximum emission has been determined quite closely. The constants corresponding to this line are $A = 2.5$ amps/cm^2 deg^2 and $\phi = 1.66$ volts. The line was observed many times: (1) in covering a tungsten filament with barium; and (2) in uncovering it from a coating of more than that giving maximum emission. The rate of evaporation of barium from the surface increases rapidly as either the relative amount of coating or the temperature are increased. At a given temperature, the logarithm of the rate is approximately a linear function of the amount of barium. The rates for the thickness giving maximum electron emission are of the order of one billionth of values from the literature for barium in bulk. For temperatures up to 1250°K, and possibly beyond, the penetration of barium into the interior of the tungsten by diffusion is slight.

75. The voltage current relation in central cathode photo-electric cells. THORNTON C. FRY and HERBERT E. IVES, Bell Telephone Laboratories, Inc.—This paper presents a theoretical basis for the interpretation of the experimental results described in the paper which follows. It considers a source of photo-electrons located on the inner of two concentric spheres; derives the trajectory of an electron shot off at any angle with any speed; and then makes use of this information to compute the current which would be received by a small collector located anywhere on the outer sphere upon very general assumptions as to the directional distribution and velocity distribution of the photo-electrons. This theoretical study is followed by graphical presentation of results computed for several typical cases of special interest in connection with the experimental study.

76. The distribution in direction of photo-electrons from alkali metal surfaces. HERBERT E. IVES, A. R. OLPIN AND A. L. JOHNSRUD, Bell Telephone Laboratories, Inc.—An experimental study of the distribution in direction of photo-electrons emitted from alkali metal surfaces irradiated by light incident at various angles and polarized in different planes. The alkali metal surfaces used were of two sorts: (1) Liquid alloys of sodium and potassium; (2) thin films of potassium or rubidium on polished platinum. In all cases the alkali metal surface was at the center of a large spherical enclosing anode, provided either with collecting tabs at various angular positions or with an exploring finger. It is found that the emission closely obeys Lambert's law, but that the ellipse by which the emission is represented, in polar coordinates, is more elongated normally to the surface for perpendicularly incident light than for obliquely, when the direction of the electric vector is in both cases parallel to the surface, and still more elongated for obliquely incident light with the electric vector in the plane of incidence. The distribution curves are all perfectly symmetrical about the normal to the surface, showing no tendency to follow the direction of the electric vector.

77. The nature of the sensitive surface of the point in a Geiger electrical counter. L. F. CURTISS, Bureau of Standards.—The metal of the point must be in a *catalytic* condition to hold the gaseous surface layer responsible for the sensitive condition. This is shown by the following

observations: 1. Points of platinum black and palladium black work as well as the usual oxidized steel or glowed platinum points. 2. *All* sensitive points are "poisoned" by the usual catalytic poisons such as mercury vapor, sulphur dioxide and hydrogen sulphide. As soon as these substances are admitted to the counting chamber the point instantly ceases to function. Only when the point is *negative* is it necessary to provide it with a sensitive surface. Any sufficiently sharp metal point will work when the point is *positive* with proper voltage. This gaseous layer therefore plays an important role in releasing the electrons from the point when negative. Two tentative explanations are proposed, one assuming an ionization of the gas layer to release the electrons after which it recombines; the other an evaporation of the gas layer with free electrons from the metal which have entered into the structures of the gas layer followed by a readsorption of the gas. Since both recombination and readsorption occur very quickly at the pressures usually used either process would restore the counter soon enough to count particles entering with any rapidity within the limitations imposed by ordinary methods of registration.

78. A close collision between an alpha-particle and a nitrogen nucleus. L. F. CURTISS, Bureau of Standards.—Approximately 83,000 α-ray tracks in air have been photographed by the method developed by Shimizu (Proc. Roy. Soc., **99,** 425 (1921)), and modified by Blackett (Proc. Roy. Soc., **102,** 294 (1922)). Many forks and bends of minor interest have been recorded. One fork involving a close collision between the α-particle and a nitrogen nucleus seems particularly important. An analysis of the photographs yields the following results: A nitrogen and not an oxygen nucleus was struck. The α-particle was deflected through an angle $\phi = 110°$ with its initial direction and travelled 10.5 mm after the collision. The nitrogen nucleus traveled 4.7 mm at an angle $\theta = 26\frac{1}{2}°$ to the original direction of the α-particle. From the equations developed by Darwin (Phil. Mag., **27,** 500 (1914)) one computes that at the moment of closest approach the α-particle was only $.5 \times 10^{-12}$ cm from the center of the nucleus. The velocity of the α-particle at the moment of impact was 1.1×10^9 cm/sec and after the impact 8.7×10^8 cm/sec. Although the α-particle has penetrated into the nuclear structure with sufficient energy to eject a proton there is no evidence from the photograph that this has occurred. This indicates that other factors than nearness of approach and energy of the impinging α-particle are involved in determining whether a disintegration occurs.

79. Increase in conductivity of glass under electron bombardment. W. R. HAM, M. W. WHITE AND H. R. KIEHL, Pennsylvania State College.—In a continuation of the study of the reflection of electrons from the target of a Coolidge x-ray tube (Ham and White, Phys. Rev., **27,** 510 (1926) and Ham, Phys. Rev. **29,** 908 (1927)) the effect of their impact upon the walls of the tube was examined. Upon connecting to the anode a metal coating shellacked to the outer walls of the tube, a current was found to flow through the glass during operation of the tube. This current varied in magnitude and direction as the retarding potential applied to the coating was varied, and was of such magnitude as might be expected from the potential applied and the resistance of the glass. Thermocouple measurements indicated at the same time the presence of a current to the anode along the inner surface of the glass, of greater magnitude than might be expected with the potential applied. Application of a retarding potential sufficient to prevent the reflected electrons from reaching the glass, caused this current as well as that through the glass to disappear. At this point the heat developed in the anode became equal within 0.2 percent to the energy input to the tube. The results indicate that during normal operation of the tube, the reflected electrons greatly increase the conductivity of the inner surface of the glass.

80. An application of vacuum tubes in measuring small alternating currents of any frequency. R. E. MARTIN, Lehigh University.—Four three-electrode vacuum tubes and a D'Arsonval galvanometer are connected in such a manner that, on passing an alternating current into the system, the tubes will function as a full wave rectifier and pass a direct current through the galvanometer. Calibration can be accomplished by passing either a known direct current or alternating current through the arrangement. The accuracy of the device has been checked by comparing the deflections of the galvanometer with the current as determined from

observations made on a Duddel thermal galvanometer through which the same current is passed. In this manner alternating currents down to the lower limit of the current sensitivity of the D'Arsonval galvanometer have been measured. The deflection of the galvanometer has been proven to be independent of the frequency up to 3,000,000 cycles and should be for any frequency. Since the deflection of the galvanometer is a linear function of the current, very small currents can be determined very accurately. For the same reason the arrangement can be calibrated by using known currents of several milliamperes.

81. The variation of effective capacity of an air condenser due to humidity and pressure changes. GEORGE D. ROCK, Catholic University of America.—The variation of effective capacity of an air condenser due to humidity change was determined by means of a heterodyne method tuning the beat note to a 1000-cycle frequency and noting balance by means of phones and a thermo-galvanometer. The condenser was placed under a bell jar and in contact with air of various degrees of dryness secured by exposure to H_2SO_4 solutions and balance restored for each case by means of a compensating condenser. Capacity change due to pressure variation was then noted and compared with that caused by humidity.

82. The positive ray analysis of ammonia. JAMES H. BARTLETT, JR., Harvard University. The ammonia molecule has been investigated by Dempster's electromagnetic method of positive ray analysis of gas ions. Two principal ions occurred, with approximately the same intensity at low pressures. These are identified as $(NH_3)^+$ and $(NH_2)^+$, respectively. At higher pressures, secondary positive ions appeared with m/e ratios of 14, 15, and 18, which are probably $(NH)^+$, N^+ and $(NH_4)^+$, with the first the strongest and the second the weakest in intensity of the three. No negative ions and very few, if any, hydrogen ions were observed. The ionization potentials of $(NH_3)^+$ and $(NH_2)^+$ were observed to be 11.2 ± 1.5 volts and 12.0 ± 1.5 volts, respectively, these values being the means of several observations. The above results furnish evidence tending to show that in ammonia electron impact with 60-volt electrons may result either in the formation of the molecular ion $(NH_3)^+$ or in the formation of the $(NH_2)^+$ ion. The primary processes probably occurring are $NH_3 = (NH_3)^+ + \epsilon$ and NH_3 $(NH_2)^+ + H + \epsilon$.

83. Structure of the violet bands of silicon nitride. F. A. JENKINS. New York University.—The spectrum of the glow produced by the reaction of $SiCl_4$ vapor with active nitrogen has been photographed with the Harvard 21-ft. grating. The structure lines of ten bands in the violet system ascribed to SiN have been measured. As predicted by Mulliken, the band structure is that characteristic of a $^2S \rightarrow {}^2S$ electronic transition, since no Q branch is observed and there is one missing line between the P and R branches. The latter show a narrow doubling for higher values of m. This doubling decreases in each sequence as n increases, but shows certain irregularities; in the (1,1) band it begins abruptly at $R(12)$ and $P(14)$. Various other perturbations are found. The combination principle is applied, and from the resulting term-differences the following molecular constants are obtained: $B' = 0.7189 - 0.01045n$; $B'' = 0.7291 - 0.00594n''$. Measurements of the heads of the (2,2), (3,3), (4,4) and (5,5) bands of the isotopic systems due to $Si^{29}N$ and $Si^{30}N$ give conclusive evidence in favor of the quantum mechanics formulation of the vibrational energy as a function of $(n+\frac{1}{2})$. The observed values for the isotopic displacements of the heads differ from those calculated with half-integral numbers by -0.031 ± 0.035, whereas they differ from those calculated with integral numbers by -0.894 ± 0.112.

84. On infra-red spectra: hydrogen chloride; the methyl halides. C. F. MEYER, A. A. LEVIN, and W. H. BENNETT, University of Michigan.—The fundamental absorption band of hydrogen chloride has been examined with narrower slits than it has been possible to use heretofore. Each line of the band hitherto observed has been separated into two lines which arise from the existence of the isotopes Cl_{35} and Cl_{37}. The wave-number separation of these lines increases in passing across the band in the direction of higher wave-numbers. A study of the spectra of the methyl halides is under way. Most of the principal regions of absorption have been located. Some of these are shown to comprise several bands. All bands which have

thus far been examined in detail fall into one of two groups. One group shows well separated fine structure. There is a three-fold succession of intensity of the maxima, in accordance with the three-fold symmetry of position of the hydrogen atoms. The other group of bands has P, Q, and R branches. The lines are closely spaced, but those of the P and R branches have been separated in some cases.

85. Beryllium hydride band spectra. WILLIAM W. WATSON, University of Chicago.—With an arc between beryllium electrodes in a hydrogen atmosphere as a source, two new band groups were photographed in the first order of the 21-foot grating. One group consists of an isolated set of twelve branches in the region 4800–5120A, with a common origin at 20031 cm^{-1}. This band, which undoubtedly belongs to the $^2P_{1,2}-^2S$ class due to MeH molecules, exhibits some unique features: the usual doublet separation at the origin is not detected since it is probably about 0.3 cm^{-1} as for the Li atom; the series all shift markedly towards the red for $j>30$. The other spectrum stretches from λ3700 into the ultra-violet and consists of a number of bands with simple P and R branches only, degraded to the red. These bands are therefore of the $^1S-^1S$ type with BeH^+ as the probable emitter. The quantum analysis gives $\nu=39059+1460.5n'-14.5n'^2-2182.0n''+41.0n''^2$ as the equation for the zero-points, and $I_0'=3.85\times10^{-40}$ gm.cm², $I_0''=2.50\times10^{-40}$ gm.cm², $\alpha'=0.1360$, $\alpha''=0.3075$, r_0(final state) $=1.29\times10^{-8}$ cm.

86. Beryllium hydride bands. MAX PETERSEN, Lehigh University.—In the spectrum of a beryllium arc run in a low pressure (5 to 15 mm) of hydrogen a strong band group is found near 5000A. Spectrograms in the second order of a 21-foot grating show that the group consists of several overlapping sets of three-branch bands, of which the earliest lines are narrow doublets. The group apparently embraces the 0,0; 1,1; 2,2; etc. parts of a band system which seems attributable to BeH. If this analysis is correct the origin of the band system is about 20032 cm^{-1}, the head of the strongest Q branch. As many as six P and R branches can be traced, the stronger of which show so great deviations from a parabolic wave-number formula that while the band is degraded toward the violet and the strongest P branch is followed to its head, the corresponding R branch is also found nearly to a convergence. From the earlier lines of the strongest P and R pair a moment of inertia of 3.53×10^{-40} and, assuming BeH origin, an internuclear distance of 1.54×10^{-8} cm are obtained. Precise measures of these bands are under way and it is planned to get useful plates of two other groups of bands which appear on small plates and may belong to the same system as the 20032 group.

87. Zeeman effect in the calcium hydride A band. P. S. DELAUP, University of Chicago. (Introduced by William W. Watson.)—The calcium hydride A band at λ7000 was photographed in the first and second orders of the 21-foot grating with field strengths from 9000 to 23,000 gauss. At low field the $Q_1(1)$, $Q_1(2)$ and $P_1(4)$ lines were found to be split into doublets having a separation twice that of the normal Zeeman separation. This is in agreement with Van Vleck's formula for the case of loose coupling of the spin axes (Phys. Rev. **28,** 1009 (1926)). The separation was found to increase linearly with the field, at least for low and medium fields. At high fields the separation of the components becomes comparable with the distance between the lines, and accurate measurements could not be made. For high magnetic fields there seems to be a tendency for the distance between the Q_1 and Q_2 branches to contract.

88. Magnetic rotation lines in the red sodium bands. W. R. FREDRICKSON, University of Chicago.—The heads of the red absorption bands of sodium have been remeasured and can be represented by the formula $\nu=15006.68+(115.22n'-0.384n'^2)-(157.14n''-0.423n''^2)$. The magnetic rotation lines in this region have been photographed at high dispersion. Practically all the lines given by Wood (Astrophys. Jour. **30,** 364 (1909)) are obtained and in addition it is found that many strong lines are accompanied by weak lines close to the strong lines. The lines in all cases are very close to absorption lines. A correlation between the absorption and magnetic rotation data has been made—assigning lines to some hundred bands. The magnetic rotation lines for the n'' progressions appear to agree more closely with the n'' progression given by Loomis (Phys. Rev. **31,** 225 (1928)) for the blue-green lines than with the

n'' progression given above—showing that the green and red systems have the same final state. It is found that the bands group themselves along several parabolas of the same curvature and not along one as predicted by the Franck-Condon theory.

89. New absorption bands in nitrogen. J. J. HOPFIELD, University of California.—The absorption spectrum of pure nitrogen was observed in the gas in amounts equivalent to .06 to 19 meters at atmospheric pressure. The well known bands at λ1450 occurred strongly, and besides these two new band systems or a system of double bands (the measurements are not sufficiently accurate to decide this) also occur in absorption. Taking the latter point of view, five double bands were observed. They are in pairs:

(0,0) λ1742.4, or 7.09 volts, intensity [10], and λ1728.4 [10];
(0,1) λ1701.4 [10], and λ1688.3 [10];
(0,2) λ1666.3 [7], and λ1650.2 [7], etc.

Two prominent isolated bands occur at λ1518.8 and λ1437.2. The bands are of a diffuse nature and hardly look like bands of a diatomic molecule; neither do they fit into the scheme of nitrogen bands. They seem, however, to be due to some modification of nitrogen and may account for some of the small critical potentials observed in nitrogen at points corresponding to this region of the spectrum.

90. The excited states of the H_2 molecule. E. C. KEMBLE, Harvard University.—Recent experimental work discloses five excited states of H_2 which dissociate adiabatically into a normal H atom and a two-quantum excited H atom. The complete problem of two such atoms interacting at large distances as 16-fold degeneracy. Half of the sixteen solutions of the problem are antisymmetric in the coordinates of the electrons and according to London give purely repulsive forces between the atoms. Triplet terms should not appear in the molecular spectrum. Four of the remaining eight solutions are symmetric in the coordinates of the nuclei, and four are antisymmetric. There is one double (degenerate) state in each group, so that there should be six distinct two-quantum states in all of which only three will combine with the normal one-quantum state. One of these has yet to be discovered. The B and C states associated with the Lyman and Werner bands may be identified with fair certainty. A theoretical calculation of the expected law of force for these states is in progress.

91. Intensities of lines in the ammonia band at 2μ, and the form of the ammonia molecule E. F. BARKER, University of Michigan.—Two types of bands have been observed in ammonia, arising from vibrations parallel to and perpendicular to the symmetry axis respectively. The former sort yield the moment of inertia A about an axis normal to the line of symmetry. The latter determine the second moment of inertia C and the distance between H atoms only to within two possibilities depending upon whether the molecule is prolate ($C=(2/3)A$) or oblate ($C=2A$). Intensity computations for the band at 2μ now reveal the latter choice as the correct one. Employing transition probabilities derived by the new mechanics, relative intensities are obtained, using both prolate and oblate cases, for each of the components of the 24 observed lines. The intrinsic spins of the H nucleii must be considered, since those molecules in which all three are similarly oriented possess a perfect threefold symmetry which excludes many transitions otherwise permitted. Satisfactory agreement between observed and computed intensities is obtained only for the oblate molecule. The distance from the N atom to the plane of the three H atoms is apparently from 1/16 to 1/10 of the distance between H atoms. The double character of the 10μ band may now be explained.

92. Fine structure of the absorption bands of crystals. H. M. RANDALL AND H. H. NIELSEN, University of Michigan.—The band at 3.5μ of $CaCO_3$ has been examined by an infra-red spectrograph of high resolving power and a fine structure developed with the lines spaced about 23A apart. The first results were found in January, 1927, in the band $Mg(OH)_2$ at 2.4μ.

93. Near infra-red absorption in certain organic liquids. JAMES W. SAPPENFIELD, Ohio State University.—The near infra-red absorption spectra of the following alcohols: methyl, ethyl, n-propyl, iso-propyl, n-butyl, iso-butyl, secondary butyl, tertiary butyl and butyric acid, cyclohexanone, pyridine, and methyl acetate have been observed in the region from

0.8μ to 2.5μ with an accuracy of about .002μ. Although the absorption of these substances has been studied by Weniger and others for the region between 2μ and 15μ, no previous observations have been made in the near infra-red except by Abney and Festing, who by the photographic method located approximately the bands at 0.915μ and 1.020μ. A glass prism spectrometer with a linear thermopile was used. The following table gives results for iso-butyl alcohol and tertiary butyl alcohol:

Iso-butyl: .915 1.020 1.192 1.395 1.509 1.562 1.682 1.873 1.919 1.955 2.039 2.089 2.370μ
Tert butyl: .910 1.023 1.179 1.241 1.402 1.477 1.515 1.550 1.670 1.712 1.809 1.867 2.104μ

Similar sets of values were obtained for the other substances investigated. Six of these bands can be fitted into an anharmonic series $\nu_n = \nu_0 n(1-nx)$ as was suggested by Ellis. The band at 1.5μ seems to be the harmonic of the band at 3.0μ found by Weniger in the same alcohols. The investigation is being extended to certain aldehydes, ketones and other acetates.

94. Combination frequencies in the infra-red spectrum of quartz. E. K. PLYLER, University of North Carolina.—Many observers have studied the infrared absorption bands of quartz and have found regions of intense absorption at about 9μ, 12.5μ, and 20μ and 26μ. The writer has considered these regions of absorption as the fundamental frequencies for the ordinary ray of quartz. By combining the fundamental frequencies six bands in the region from 3μ to 9μ are accounted for. Two bands not previously observed have been found at 2.72μ and 3.18μ. The frequencies of these two bands correspond to two combinations of the fundamental frequencies. This gives a total of twelve absorption bands for the ordinary ray of quartz extending from 2.72μ to 26μ. The frequencies of the observed bands correspond with only small differences to the calculated values.

95. The effect of x-rays on the infra-red absorption of kunzite and hiddenite. P. L. BAYLEY, Lehigh University.—The range of measurement of the spectral transmission of kunzite and hiddenite, before and after exposure to x-rays, has been extended to 4.5μ to cover the entire region of transmission of the samples (0.3 to 4.5μ). Previous measurements (Phys. Rev. **29**, 353, 1927) with a glass prism showed absorption bands in radiated kunzite at 0.625, and 0.910. Hiddenite had bands at 0.625 and 1.0μ and 1.67μ. Measurements on the same samples with a rock salt prism confirm the presence of those bands and absence of the one at 1.67μ in radiated kunzite. Although both have much the same absorption from 0.45 to 1.3μ, there is little similarity beyond 1.3μ. Beyond the band at 1.67μ the transmission of hiddenite rises to a maximum at 2.1μ, drops rapidly to a low value, rises slightly at 4.0μ and decreases sharply toward zero beyond 4.4μ. Kunzite shows more absorption after radiation than before radiation but this difference decreases steadily to zero at 3.7μ. Throughout the region where there is a difference, both show the same slight absorption bands at 1.4, 1.85, 2.15, 2.5, 2.65 and 3.1μ. Beyond 3.7μ their identical values decrease rapidly, increase slightly at 4.0μ, and decrease sharply toward zero beyond 4.3μ.

96. Multiplet separations for equivalent electrons and the Röntgen doublet law. S. GOUDSMIT, University of Michigan.—Expressions can be derived for the separation of multiplets arising from configurations of equivalent electrons. Those explain why the Röntgen doublets obey the Sommerfeld formula, although this formula was derived formerly for one single electron only. The separations of more complicated multiplets are connected also with the Sommerfeld formula. According to Landé the multiplet separations can be characterized by factors, designated by Γ, which give the displacement of each level from the center of gravity of the whole multiple level. The properties of these Γ factors can be shown to be quite analogous to the well-known properties of the magnetic separation factors, g, introduced by Landé for the explanation of the Zeeman effect. There exist a Γ sum rule, corresponding to the well-known g sum rule, stating that, for given quantum numbers of the electrons, the sum of the Γ values belonging to a certain total moment j is a constant, independent of the type of coupling of the electrons. This rule is important especially because it makes it possible to obtain expressions for the multiplet separations in general cases.

97. The natural resonant frequencies of a quartz sphere. K. S. VAN DYKE, Wesleyan University.—By means of the piezo-electric property of quartz a number of spheres of different sizes are driven as resonators and the principal natural frequencies of the sphere determined. The cathode-ray oscillograph is used (as previously described (Phys. Rev. **31**, 302 (1928)) to make certain that the sphere is vibrating at the fundamental frequency of the driver and not at some harmonic. For the spheres used (diameters about 1 cm and 5 cm), the characteristic frequencies are found to be in the ratios 1, 1.47, 1.61, 1.83, 2.12, 2.18, 4.12, etc., where the lowest frequency corresponds to a radio wave-length of about 108 meters per mm diameter. While the elastic moduli of crystalline quartz are known for any direction in quartz, the mathematical problem of using these constants to determine the vibration frequencies for a sphere of crystalline quartz is hopelessly complex. The attempt has been made to identify the geometry of the mode of vibration by observing the Giebe and Scheibe type of glow discharge around the sphere in vacuum. The glow is characteristic of the mode and for some modes has shown nodal lines in easily recognizable patterns.

98. The force equation and some related theorems in wave mechanics. ARTHUR EDWARD RUARK, Mellon Institute, University of Pittsburgh, and Gulf Production Company.—Ehrenfest (Zeit. f. Phys., **45**, 455 (1927)) gave a generalization of Newton's force equation which holds for conservative systems in wave mechanics. Let Ψ be the wave function; Ψ^*, its complex conjugate; V, the classical potential energy function; x_n, a Cartesian coordinate of a particle of the system; $\bar{x}_n$, the corresponding coordinate of the centroid of the $\Psi\Psi^*$ distribution; m_n, the mass of the particle in question; and $d\tau$ the element of volume in the coordinate space. The generalization of Newton's law is $m_n d^2\bar{x}_n/dt^2 = \int \Psi\Psi^*(-\partial V/\partial x_n)d\tau$. A proof of this relation is presented for systems obeying the wave equation $\Delta\Psi - 8\pi^2 V\Psi/h^2 - (4\pi i/h)\cdot \partial\Psi/\partial t = 0$. From this relation theorems analogous to the virial theorem, and other laws of ordinary mechanics, are easily obtained.

99. On the origin of the Aurora Borealis. E. O. HULBURT, Naval Research Laboratory, Washington, D. C.—It has been assumed by Birkland, Strömer, Vegard and others that the aurora is caused by charged particles from the sun which are diverted to the polar regions by the magnetic field of the earth. There are possible objections to this; namely, if the charged particles are α-particles or ions of some sort they do not combine a sufficient penetrating power with a sufficient magnetic deflectibility to explain the height and structure of the aurora, and if they are electrons their penetrating power may be too great. It is therefore suggested that the aurora is due to ultraviolet light of the sun which produces ions and electrons in the high atmosphere of the earth, above 200 km or so. These diffuse along the magnetic lines of force, concentrate at the magnetic poles of the earth, recombine and in some way yield up their energy to form the aurora. The aurora illumination during the strong display of August 20, 1927, was observed to be somewhat weaker than the light of the crescent moon, and from this the total energy of the aurora was estimated to be 10^{15} erg sec^{-1}. This is in rough agreement with the energy of the upper spray of photo-electric ionization in the high atmosphere indicated by wireless telegraphy, according to some recent calculations.

100. Wave-length measurements in the arc and spark spectra of hafnium. WILLIAM F. MEGGERS, Bureau of Standards.—Using samples of hafnium salts presented by Professors Bohr and Hevesy, the arc and spark spectra characteristic of this element were photographed with concave-grating and quartz-prism spectrographs. Wave-length measurements were made on about 2100 lines, but 609 of these were discarded as impurities, identified mainly as columbium, zirconium, and titanium. Nearly 1500 lines remain to describe the hafnium spectra between the wave-length limits 2155.72A in the ultraviolet and 9250.27 in the infrared. In this investigation an attempt has been made to improve upon an earlier description of these spectra (1) by extending observations to shorter and to longer waves, (2) by increasing the precision of the wave-length measurements to 0.01A, and (3) by making a more critical differentiation between lines characterizing neutral atoms (Hf I) and those ascribable to ionized atoms (Hf II). Comparison of these results with the earlier measurements of zirconium spectra proves that hafnium was invariably present as an unrecognized impurity. The most

sensitive Hf I and Hf II lines for spectrochemical identification are tentatively selected. The stronger Hf II lines are identified with faint Fraunhofer lines in the sun's spectrum.

101. Poisson diffraction on disks of colloidal dimensions. R. A. WETZEL AND GEORGE NEEDHAM, College of the City of New York.—In a dark field ultra-microscope we have observed images of colloidal gold, rubber latex, silver and rutile with a more or less sharp dark spot in the middle of a bright disk of light. For macroscopic objects Arkadiew (Phys. Zeit. **14**, 832 (1913)) records similar images. The effect has been photographed for silver and rutile particles as small as one-half the wave-length of yellow light.

102. The dielectric constants of silver sols when diluted with varying amounts of ethyl alcohol. GEORGE D. ROCK AND SIMON KLOSKY, Catholic University of America.—In order to determine the charge on colloid particles, it is customary to measure the velocity at which they migrate under the influence of a known difference of potential. In the formula which shows the relation between these two quantities, the dielectric constant appears. It is usual to consider the dielectric constant of the sol equal to the dielectric constant of the medium; but as this is not always true (for example, vanadium pentoxide) it was thought desirable to measure it in the case of silver sols especially in the presence of varying amounts of alcohol. The dielectric constants were then determined by means of a heterodyne method and found to be substantially equal to the dielectric constants of the dispersion media.

103. Critical potentials below 4.7 volts for negative ion formation in mercury vapor. WALTER M. NIELSEN, Duke University.—The experimental apparatus and procedure is given in another paper presented at this meeting. At higher vapor pressures, the following critical potentials below 4.7 volts were observed: .4, .8, 1.4, 1.8, 2.3, and 2.7 volts. They are believed to be due to the mercury molecule. The magnitude of such negative ion currents increases more rapidly than the first power of the vapor pressure. Only those formed at about 2.3 and 2.7 volts are measurable at low vapor pressures such as in the paper referred to above. There is evidence that the number of negative ions formed per unit electron current increases more rapidly with increase of vapor pressure for driving potentials of .4, .8, and 1.4 volts than for those formed at 2.3 and 2.7 volts and all of the atomic critical potentials discussed in the former paper. The negative ions formed at the lower voltages are especially prominent when liquid mercury is present in the tube. It is probable that critical potentials lower than .4 volt may be found as the pressure is further increased.

104. The electron wave theory of electrical conductivity. WILLIAM V. HOUSTON, Institut für Theoretische Physik, Munich.—The quantum statistical treatment of an electron gas is justified by the picture of an electron as a standing wave; consistently to use this idea in a conduction theory it is necessary to treat the interaction between the electron waves and the metallic ions as an interference phenomenon. This can be done by using the results of the work on x-ray diffraction. This treatment, in connection with Sommerfeld's work on the electron gas, gives directly the dependence of the electrical conductivity on the temperature in very close agreement with experiment. With a reasonable assumption as to the field of an ion, it is possible to compute roughly the magnitude of the conductivity, the sudden drop of conductivity and change of temperature coefficient at the melting point, the effect of pressure, the dependence of the conductivity upon direction in a single crystal, and the thermoelectromotive force in a single crystal. The advantage of this treatment, however, lies not only in the number of phenomena which it correlates, but in the fact that all the assumptions involved have already been found necessary for other purposes.

105. A discussion of the fraction of mass of a spring that is accelerated in simple harmonic motion in the case of various types of conically wound springs. O. B. ADER, Duke University. (Introduced by G. D. Collins.)—A determination of the extension of a conically wound spring under a given load in terms of the constants of the spring is necessary to the solution. The equations in Cartesian coordinates for a curve which conforms to our definition of a conically wound spring are used in this determination. Our result is, $Z = 2Wa^2L^3/3\pi nb^4$ where Z is the

extension under the load W, L is the length of the wire, n the modulus of rigidity, b is the radius of the wire, and a is a constant approximately equal to R/L for springs of the type treated, R being the maximum radius of the conically wound spring. (The corresponding equation for the helical spring is, $Z=2WR^2L/\pi nb^4$.) This same equation is developed by a second method from energy considerations. Now using the formula, $K.E.=\frac{1}{2}\int_0^L \dot{x}^2\rho ds$ where $\dot{x}$ is the velocity of the ith particle of the spring, ρ is the mass per unit length, and ds is an element of length measured along the wire, we can readily calculate that one-seventh of the mass of the spring enters into the equation for its kinetic energy,—as compared to one-third for the helical spring. Solutions have also been obtained for the inverted conically wound spring, truncated, inverted truncated, and double conical, each of which presents various degrees of complication.

106. The dielectric constant and electric moment of CO, CS_2, COS, and H_2S. C. T. ZAHN AND J. B. MILES, JR., Princeton University.—In view of the interest in the structure of CO with reference to its infra-red spectrum, it was thought important to obtain the electric moment of CO and associated molecules from the variation of dielectric constant with temperature as given by the Debye Equation. The improved heterodyne null method previously described, was used to measure the dielectric constants of carefully purified gases over various ranges of temperature. The results are represented very well by the Debye Equation $(\epsilon-1)vT=AT+B$, where ϵ is the dielectric constant and T the absolute temperature, and v the specific volume. The values for A are .000670(CO), .002790(CS_2), .001970(COS), .001223(H_2S); and for B .0078(CO), .089(CS_2), .352(COS), .722(H_2S). These values of B give for the electric moment in c.g.s.e.s. units $\times 10^{18}$; .10(CO), .326(CS_2), .650(COS), .931(H_2S). The moment of CS_2 indicates a different structure from that of CO_2 whose moment is probably zero. H_2S was measured in order to make a comparison with the recent work of Braunmuehl.

107. New features of the red band system of Na_2. F. W. LOOMIS AND S. W. NILE, JR. New York University.—On photographing the Na_2 absorption spectrum with a neocyanine plate it was found to terminate in a sharp edge at 12400 cm^{-1}. This represents an unusual feature of the Franck-Condon intensity distribution and is shown to be due to the fact that $\omega_0'' > \omega_0'$ and $B_0'' > B_0'$ but $D'' < D'$, D being the heat of dissociation. B_0' and α' were estimated from Birge's semi-empirical rules that B_0/ω_0 and $2xB_0/\alpha$ are nearly constant during a transition, by comparison with the green system. The potential energy curves could then be drawn and the Franck-Condon locus of maximum intensity plotted. The calculated infra-red edge came at 12000 cm^{-1}. The same calculation shows that the red system should also have a short wave-length edge in the green, and this is apparent in the spectrum when the vapor is dense. The form of the potential energy curves shows that although $\omega_0'' > \omega_0'$ and $B_0'' > B_0'$, the reverse is the case when n is high, and $\omega_n'' < \omega_n'$ and hence $B_n'' < B_n'$. Consequently, as one proceeds away from the system origin, the R heads separate from the Q heads and the latter become prominent. Finally the bands even degrade to the violet. This accounts for the observed discrepancy between magnetic rotation and absorption data, since magnetic rotation lines should occur at R heads, but not at Q heads.

108. Voltage-intensity relations of twenty-nine lines of the mercury spectrum. PAUL B. TAYLOR, University of Pennsylvania.—Data are given for the variation in intensity with voltage of 29 lines of the mercury spectrum between 2378 and 4108A. A photographic method of measurement was used. It is to be noted from the graphs that at lower voltages the curves for members of the same series have very different slopes which increase with m number. Indeed, for low values of m the intensity may even decrease with rising voltage. At higher voltages the curves of one series approach parallelism. As the m numbers increase the distance between curves grows less approaching a limiting position corresponding to the limit of the series. Curves of the same triplet lie close together; in some cases they are identical within the precision of measurement but in other cases they are distinctly different, for example 3341 and 2894, 2803 and 2482. Athanasiu reported that 2652, 2967 and 3025 all maintained the same relative brightness under conditions quite similar to those of the present experiments. This is in disagreement with the present results.

109. Dielectric losses by a calorimetric method. G. E. OWEN, University of Pennsylvania. —Small condensers of fibre, rubber and fused quartz, were put into an oscillating circuit and the dielectric losses measured by a differential calorimeter. In a vulcanized fibre condenser one centimeter square, .03 centimeter thick, with plates applied by the Schoop pistol process, the losses bear a linear relation to the frequency from 250 to 600 kilocycles: and are proportional to the voltage squared up to 50 volts. Above 50 volts the results are not consistent. At 30 volts the losses vary from .013 watts at 250 kilocycles to .021 watts at 600 kilocycles. A condenser kept at 70 percent relative humidity shows about twice as much loss as one kept for two days in a bottle containing phosphorous pentoxide. If the condenser is kept in this drying atmosphere, the losses diminish slowly for several weeks. For a condenser of soft rubber, similar results were obtained, which are consistent up to 85 volts. A clear fused quartz tube gave small but measurable losses. It will be used as a standard. The voltages were measured with an electrostatic voltmeter. A peak vacuum tube voltmeter did not seem to be independent of frequency. The work is being continued with glass, mica and celluloid.

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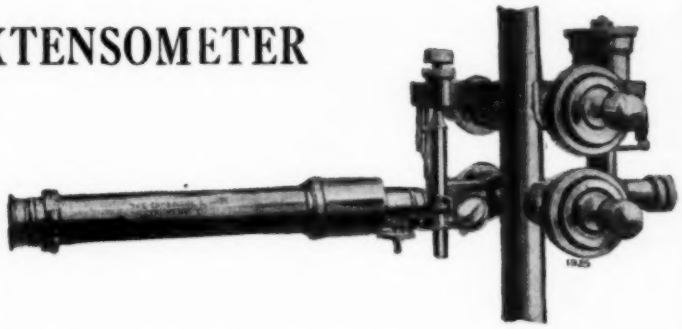

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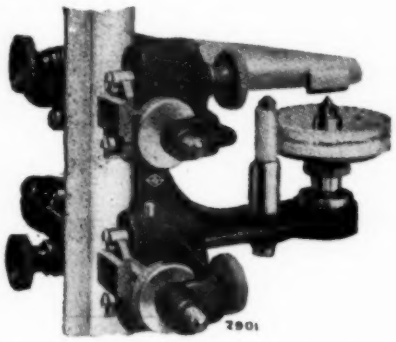

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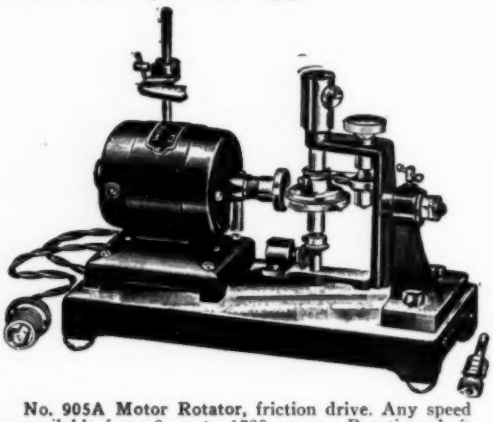

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Our best enclosed-dial boxes are Nos. 4780, 4782 and 4784. They are suitable for D.C. and for A.C. frequencies up to 50,000 cycles. They have one contact per dial, back brush contact being bridged by a copper spiral. Dials cannot be turned inadvertently from maximum to zero resistance. Each dial has 9 coils wound on non-metallic spools; solid nickel switch studs, bakelite top plates, mahogany boxes.

CHARACTERISTICS

List No.	Dials	Values (ohms)	Accuracy (per cent)		Price
			all but 0.1 ohm coils	0.1 ohm coils	
4780	4	9(1+10+100+1000)	0.05	—	$60.00
4781	4	9(10+100+1000+10000)	0.05	—	70.00
4782	5	9(0.1+1+10+100+1000)	0.05	0.5	75.00
4783	5	9(1+10+100+1000+10000)	0.05	—	85.00
4784	6	9(0.1+1+10+100+1000+10000)	0.05	0.5	100.00

Our most popular resistance boxes are Nos. 4770-4776 inclusive. Each dial has 9 steps and a zero point; all coils wound on non-metallic spools. Solid nickel switch studs, hard rubber top plates, mahogany boxes. Dials can be set for any value without turning switches more than 90 degrees.

CHARACTERISTICS

List No.	Dials	Values (ohms)	Accuracy (per cent)		Price
			all but 0.1 ohm coils	0.1 ohm coils	
4770	2	9(1+10)	0.1	—	$25.00
4771	2	9(10+100)	0.1	—	25.00
4772	2	9(100+1000)	0.1	—	25.00
4773	3	9(1+10+100)	0.1	—	33.00
4774	3	9(10+100+1000)	0.1	—	33.00
4775	4	9(1+10+100+1000)	0.1	—	40.00
4776	4	9(0.1+1+10+100)	0.1	1	40.00

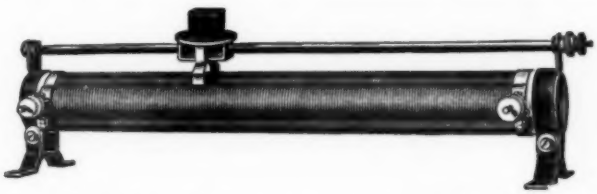
Send for Catalog P-40

LEEDS & NORTHRUP COMPANY
4901 STENTON AVENUE, PHILADELPHIA

LEEDS & NORTHRUP

Galvanometers
Potentiometers
Bridges and Resistance
Condensers and Inductance
Testing Sets
Recording and Controlling Pyrometers
Pumps and Hoists
Electric Heat Treating Furnaces
Instruments for Measuring and Controlling Conductivity of Electrolytes and Hydrogen Ion Concentrations

G-68B



Jagabi Laboratory Rheostats

Standardized in 57 different ratings

There are three sizes of the tube rheostats with length of 8, 16, and 20", respectively, which are wound with various sizes of resistance wire or strip. Resistance values may be had as high as 30,000 ohms, with current capacity of 0.1 amperes; and as low as 0.34 ohms with current capacity of 25 amperes.

Also we supply "single," "vertical," "double," "universal" and "Dodge" design Rheostats, as well as screw-driven fine adjustment Rheostats of the same types, and Compression Carbon Rheostats for regulating high current.

A new design of Non-Inductive Rheostat is now available which is important in high frequency work.

Write for descriptive Catalog 1140-P

JAMES G. BIDDLE
Electrical and Scientific Instruments
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Taylor Process Fine Wires

(Patent Applied For)

THE TAYLOR PROCESS for making wires from substances which lack ductility, consists in melting the material in a glass or quartz tube and drawing down to the required size. The process has been so developed that a great many non-ductile substances can now be drawn into wire by it. The elements or alloys, because the drawing is done in glass or quartz, are in a very pure state, although lengths of more than a few feet cannot be obtained. The wires may be had with or without the glass insulation.

We make Taylor Process wire of Pt, Pd, Rh, Au, Ag, Cu, Fe, Co, Ce, Zn, Cd, Ge, Pb, Sb, Bi, Sn, Se, Te, Tl, Ga, and In, Constantan, Bi-Sn, Cd-Sb (alloy where large E. M. F. is desired) and many other alloys. Our wires are packed in containers holding one foot and with few exceptions, the sizes are from one mm to one micron. We manufacture too, fine wire by the Wollaston Method, by extrusion and by bare drawing.

Whenever you need wire from unusual materials or in unusual sizes, write us. Very probably we can supply you.

BAKER & CO., INC.
54 Austin St., Newark, N. J.

New York San Francisco Chicago

An improved Vacuum Gauge

A Steel Frame

Not only very rigid in construction, but neat in appearance and possessing a finish that can easily be kept clean.

A Metal Scale

Very easy to read, because of the black background and white calibrations, which also give it a good appearance. Strong, durable, not affected by moisture, and easily adjusted.

An Overflow Chamber

A very important improvement. This chamber, located at the upper end of the mercury reservoir, prevents accidental spilling of the mercury. In case the plunger should be pushed down when there is no vacuum on the gauge, the mercury displaced by the plunger will flow into this chamber.

General Electric is glad to assist investigators having special problems the solution of which may be facilitated by knowledge of equipment and processes developed through G-E research. To avail yourself of this service, address Special Products Section, Schenectady.

840-5

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Give your students the advantage of observing visually wave forms of electric circuits.

Show them the effect of inductance and capacitance introduced in the circuit.

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These, and many other similar aids to teaching electricity, and periodic physical phenomena are made available now by the new Stabilized Cathode-Ray Oscilloscope.

Portable and always ready for use by simply connecting to the desired source.

Described in A.I.E.E. Journal, June, 1927. Write for Reprint and Circular No. 273.

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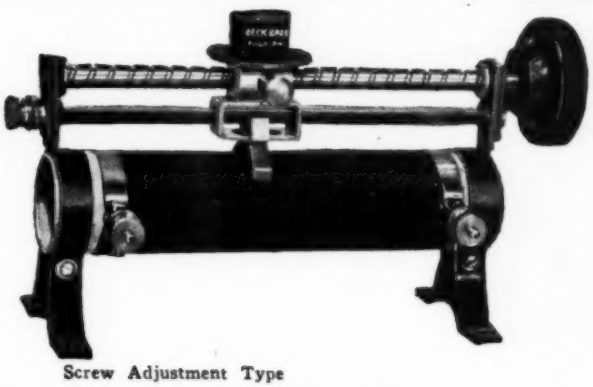
California Institute
of Technology

BECBRO
Laboratory Rheostats



Screw Adjustment Type

"BECBRO" Rheostats carried in stock include numerous ratings.

Included in the stock sizes are tubular types of length 20"; 16"; 8"; the resistance element being Wire or Ribbon.

Each tube has a slider adjustment which varies the resistance by very small steps from Zero to total value of the unit.

The approximate total resistance of these stock rheostats vary from 0.3 ohm to 30,000 ohms per unit, and have corresponding current capacities of 25 amperes down to 0.1 ampere.

Rheostats of more or less special construction include the Single Tube equipped with two rods and two sliders; Single and Double Tube equipped with Screw Adjustment (see cut); Double and Triple Tube mounted as a Unit; Non-Inductive Wound Tubular and Stone Types.

"BECBRO" Carbon Compression Rheostats with corresponding Normal Ratings of 250; 1000; 1500; 3000 Watts.

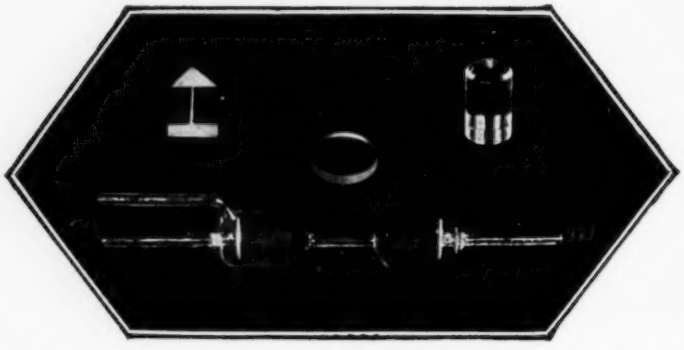
Write for Catalog P-20

BECK BROS.

421 Sedgley Ave. Philadelphia, Pa.

VITREOSIL

(Fused Pure Quartz)



OPTICAL ACCESSORIES

are especially recommended to the builders of precision instruments, and to physicists requiring the utmost accuracy.

Vitreosil spectrum tubes are particularly suited for interference measurements of wave-lengths in various metallic spectra; as a splendid source of monochromatic light in optical testing and research; to supplement laboratory analyses; and for the detection of impurities in raw materials, etc.

They are extremely efficient and can be made to emit light of great intensity without appreciable heating or electrical evaporation of electrodes. Tubes after long service will not show any signs of electrode disintegration or gas occlusion.

MADE IN FOUR STYLES

		Price each empty
Type A.	With Platinum Disc Electrodes (Illustrated Above)	$119.25*
Type B	With Aluminum Disc Electrodes	$ 30.00
Type C	With Aluminum Rod Electrodes	$ 27.00
Type D	Electrodeless	$ 10.00

* Subject to the market price of platinum

Ground and polished vitreosil discs transparent to ultra-violet and infrared rays may be used for sight windows in special research apparatus, interferometers, etc., lenses for focusing light in spectroscopic optical systems, and for photography of objects utilizing the extreme as well as near ultraviolet, also vitreosil prisms for bending light in similar applications where freedom from distortion under temperature changes is essential.

Owing to the wide range of requirements, vitreosil lenses and prisms are usually made up in accordance with buyer's specifications. Spectrum tubes as listed can, however, be supplied promptly from stock.

Write stating requirements

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QUARTZ SPECTROGRAPHS

L250. Quartz Spectrograph

Gaertner All-Metal Design

L250 Quartz Spectrograph, designed for photographing emission and absorption spectra from 800 mu mu to 185 mu mu. It takes a standard size 5¼ x 4¼ plate on which a series of exposures can be taken one below the other.

Because of its extremely compact design and substantial construction, good definition and the great photographic speed, the instrument is found to be extremely valuable in making rapid survey of spectra. Fitted with slit jaws of stainless steel.....$315.00

L250b Photographic Wavelength Scale.....$18.00

L250-W Quartz Spectrograph, the same in general specifications as L250, with the exception of a wavelength scale specially ruled built-in (similar to our larger spectrographs) and which can be photographed onto the photographic plate.....$400.00

L253 Quartz Spectrograph, Littrow Auto-Collimating Type

High grade, automatic setting, all-metal quartz spectrograph designed for photographing spectra in three sections from 800 mu mu to 210 mu mu on standard size plate 10" x 2¼", giving a spectrum of about 600 mm long.

The compact design and the extremely substantial all-metal construction has been found of decided advantage both from the standpoint of wear and permanency of adjustment. The superiority of these spectrographs may readily be inferred from the fact that a number of instruments furnished to the leading industrial and research organizations throughout the United States, and which are in continued daily use making the routine quantitative chemical analysis for years, are giving highly satisfactory service.

Full particulars regarding these instruments with sample spectrograms on request.

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A battery and rheostat are connected in series with the electromagnet at the top of the fall apparatus and a battery switch enables the operator to release the weight at will.

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